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SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION

COMMUNICATION 10. THERMAL STABILITY OF UREA PERHYDRATE

S. Z. Makarov and B. A. Lebedev

In an investigation of the ternary system $CO(NH_2)_2 - H_2O_2 - H_2O$ by the solubility method [1], the conditions were found for the formation in this system of the compound $CO(NH_2)_2 \cdot H_2O_2$, urea perhydrate, known in industry under the name of Hyperol. The compound synthesized was carefully purified and has now been subjected to thermal analysis and investigated systematically in order to determine its stability at various temperatures.

EXPERIMENTAL

The heating curves were determined over the temperature range 20–150° with a Kurnakov recording pyrometer having a differential thermocouple. The curves obtained for the heating of urea (Fig. 1) are characterized by a single endothermic effect at 132–133°, which corresponds to melting.

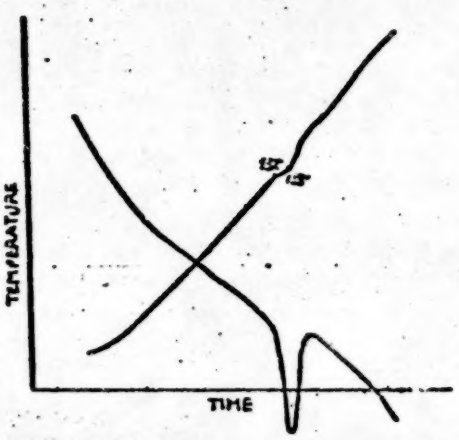

Fig. 1

The form of the heating curve of $CO(NH_2)_2 \cdot H_2O_2$ is quite different. At 64° urea perhydrate begins to decompose, and at 67° this process is accompanied by a marked exothermic effect. As a result of the heat evolved in the decomposition of the H_2O_2 eliminated, the temperature of the sample rises rapidly to 110° (Fig. 2). The differential heating curves for the compound $CO(NH_2)_2 \cdot H_2O_2$ are quite analogous in form to curves that we have given in previous papers for the thermal decomposition of perhydrate compounds. The heating curves that we have obtained confirm the presence of H_2O_2 chemically bound to $CO(NH_2)_2$ in the compound $CO(NH_2)_2 \cdot H_2O_2$.

Thermal Stability of $CO(NH_2)_2 \cdot H_2O_2$. The investigation of the thermal stability of $CO(NH_2)_2 \cdot H_2O_2$ is of practical interest, for this compound is one of the few perhydrate compounds of industrial importance. As is well known, urea perhydrate is readily soluble in water and its H_2O_2 content is about the same as that of perhydrol (30% hydrogen peroxide); it is widely used for medical and cosmetic purposes.

The thermal stability of $CO(NH_2)_2 \cdot H_2O_2$ has not been given adequate attention in the literature, except in a paper by J[illegible] [2], who gives an upper stability limit of 85°, without any indication of the method by which this value was obtained. When hermetically sealed under ordinary conditions the compound $CO(NH_2)_2 \cdot H_2O_2$ is a fairly stable substance, but when the temperature is raised to 40° and higher the stability falls appreciably and continuous decomposition sets in with evolution of oxygen.

The stability of $CO(NH_2)_2 \cdot H_2O_2$ was investigated in the laboratory under isothermal conditions over the temperature range 45–70° and at pressures of 760 and 20 mm, several parallel experiments being carried out for times up to 60 hours. The weights of the samples fell in a regular manner, owing to the loss of oxygen and water; the loss was calculated as a percentage on the weight of the sample (0.3–1.6 g).

The results of investigations at 55°, 60°, 65°, and 70° (760 mm) and at 40°, 45°, 50°, 55°, and 60°, (20 mm) on the thermal stability of $CO(NH_2)_2 \cdot H_2O_2$ are given in the table and are shown graphically in Fig. 3. The decomposition curves for 760 mm and the temperatures indicated are almost linear for times up to 20 hours. On the other hand, the decomposition curves obtained at a residual pressure of 20 mm have appreciable curvatures, and at 40° and 45° the process tends to slacken off gradually. Above 50° (20 mm) decomposition is very vigorous: the

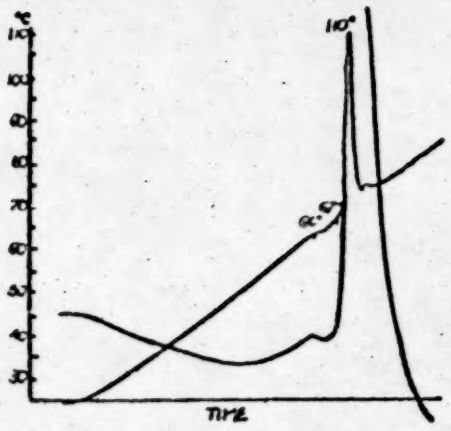

Fig. 2

decomposition curves are slightly curved, but are almost linear at first. The effect of reduced pressure is considerable, but its effect is mainly associated not with loss of active oxygen, but with removal of hydrogen peroxide and water formed in the decomposition.

An examination of the total loss (as a percentage of the amount of $CO(NH_2)_2 \cdot H_2O_2$ originally taken) indicates that reduction in pressure from 760 mm to 20 mm is similar in effect to a rise in temperature of about 25°. At both pressures increase in temperature is accompanied by more intensive decomposition of $CO(NH_2)_2 \cdot H_2O_2$ (increase in the slope of the curve).

An examination of the mean rate of overall decomposition of $CO(NH_2)_2 \cdot H_2O_2$ in the first stage of the process, in which the curves are almost linear, indicates, as the graphical representation in Fig. 4 shows, that there is a rapid decrease in the

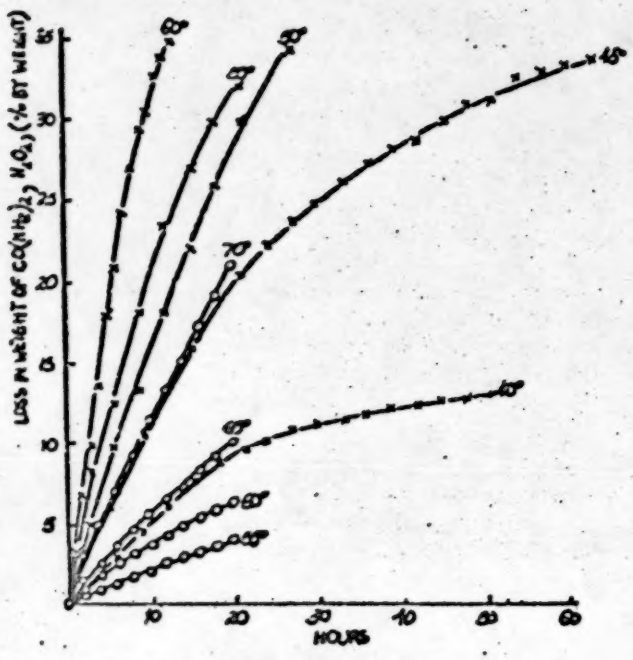

Fig. 3. x) 20 mm pressure; o) 760 mm pressure.

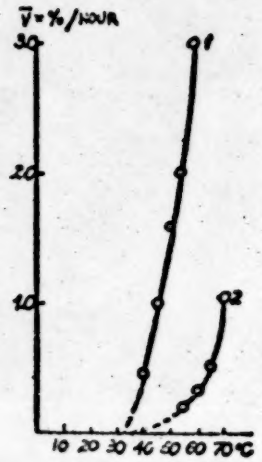

Fig. 4. 1) 20 mm pressure; 2) 760 mm pressure.

rate of decomposition of $CO(NH_2)_2 \cdot H_2O_2$ as the temperature falls, particularly at the lower pressure, 20 mm. We may suppose tentatively that the compound $CO(NH_2)_2 \cdot H_2O_2$ will have adequate stability below 30°. Observations on samples of $CO(NH_2)_2 \cdot H_2O_2$ that have been kept at room temperature confirm this supposition.

DISCUSSION OF RESULTS

The process of thermal decomposition of urea perhydrate, as can be seen from an examination of the thermal curve (Fig. 2), is evidently associated with the elimination of an H_2O_2 molecule and its decomposition into H_2O and O_2 in accordance with the equations:

$$CO(NH_2)_2 \cdot H_2O_2 \rightarrow CO(NH_2)_2 + H_2O_2$$

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2} O_2 \text{ exothermic reaction}$$

$$CO(NH_2)_2 \cdot H_2O_2 \rightarrow CO(NH_2)_2 + H_2O + \tfrac{1}{2} O_2 \text{ overall reaction}$$

The rate of formation of carbon monoxide can be calculated by two independent means: 1) graphical differentiation of the curve for the accumulation of carbon monoxide (Curve 2), and 2) from the specific activity of formaldehyde and the rate of change with time of the actual activity I_{CO} of carbon monoxide.

If, in fact, the carbon monoxide is formed exclusively from formaldehyde, the change in the actual activity of carbon monoxide in unit time must be equal to the rate of formation of carbon monoxide multiplied by the specific activity of formaldehyde.

Thus

$$\frac{dI_{CO}}{dt} = a_{CH_2O} \cdot w_{CO},$$

so that

$$w_{CO} = \frac{1}{a_{CH_2O}} \cdot \frac{dI_{CO}}{dt}. \qquad (2)$$

TABLE 1

Variation of the Concentrations and Actual Activities of Formaldehyde and Carbon Monoxide with the Time spent by the Reaction Mixture in the Reaction Zone at 670°. (Specific activity of labeled formaldehyde a_{CH_2O} = = 0.5 microcurie/mmole, actual activity $I_{CH_2O} = 1550 \cdot 10^{-5}$ microcurie/liter)

Time of contact (seconds)	Amount of CH_2O supplied (mmole/liter)	Concentration of CH_2O (mmole/liter)	Concentration of CO (mmole/liter)	Actual activity of CH_2O, I_{CH_2O} ($\times 10^{-5}$ microcurie/liter)	Actual activity of CO, I_{CO} ($\times 10^{-5}$ microcurie/liter)	Total activity $I = I_{CH_2O} + I_{CO}$	Departure from amount supplied (%)
0.021	0.024	0.094	0.22	–	–	–	–
0.024	0.031	0.110	0.24	1210	282	1492	– 4
0.039	0.024	0.187	0.22	–	–	–	
0.043	0.031	0.174	0.34	987	803	1793	+15
0.056	0.036	0.231	0.32	660	915	1573	+ 1.4
0.074	0.026	0.290	0.53	–	–	–	
0.077	0.044	0.300	0.54	408	1300	1708	+10
0.083	0.031	0.281	0.60	308	1625	1933	+25
0.091	0.023	0.350	0.66	–	–	–	
0.127	0.041	0.386	1.20	53	1655	1697*	
0.180	0.027	0.350	1.53	–	–	–	

* $I = I_{CH_2O} + I_{CO}$ has only a tentative value since at this point the specific activity of formaldehyde is close to zero.

Table 2 gives rates of consumption of formaldehyde k $[CH_2O]$ and rates of formation of carbon monoxide, calculated graphically by differentiation of the kinetic curve for the accumulation of carbon monoxide, and also by Equation 2. The rate of change of the actual activity of carbon monoxide with time dI_{CO}/dt was calculated by graphical differentiation of the curve expressing the dependence of the actual activity of carbon monoxide on time Fig. 2). As can be seen from Table 2 within the limits of experimental error the rates of consumption of formaldehyde are equal to the rates of formation of carbon monoxide. Hence, this method also leads to the conclusion that the process occurs in the successive stages: methane → formaldehyde → carbon monoxide.

The next stage of this work will be the establishment, with the aid of the kinetic tracer method, of the mechanism by which carbon dioxide is formed, and also of the part taken by methanol in the mechanism of the oxidation of methane, for, as reported in the literature, in the oxidation of methane in presence of a nitrogen oxide catalyst, not only formaldehyde, but also methanol is formed.

Owing to the thermal effect (overheating, since the decomposition of H_2O_2 takes place with evolution of heat), evolution occurs not only of oxygen, but also of water in an amount that is the greater, the higher the temperature and the lower the residual pressure. In other words, oxygen is evolved and the $CO(NH_2)_2 + H_2O$ remaining undergoes dehydration. If only oxygen was evolved in the process, then the theoretical loss for $CO(NH_2)_2 \cdot H_2O_2$ could not exceed 9.5%, whereas at 65° (760 mm) and at 45°, 50°, or 55°, or 65° (20 mm) the actual losses are higher than this, even in the course of 20 hours. For the complete dehydration of chemically pure $CO(NH_2)_2 \cdot H_2O_2$, however, the total loss of $O_2 + H_2O$ would be 30.1% on the assumption that the completely dry $CO(NH_2)_2$ remains completely unaffected. Actually, however, partial decomposition of the compound $CO(NH_2)_2$ occurs. Nevertheless, at low temperatures (below 20—30°) urea perhydrate decomposes extremely slowly under hermetic conditions, and it may be preserved for a long time, even without the addition of special stabilizers.

TABLE

Thermal Decomposition of $CO(NH_2)_2 \cdot H_2O_2$ (expressed as percentage loss in weight)

Time (hours)	Temperature (°c)							Pressure (mm)	Mean rate of decomposition (percent per hour)
	40	45	50	55	60	65	70		
2				0.46	0.97	1.18	2.66	760	$\bar{v}_{55} = 0.196$
4				0.89	1.81	2.35	4.82	760	$\bar{v}_{60} = 0.322$
6				1.15	2.43	3.40	7.01	760	$\bar{v}_{65} = 0.499$
8				1.65	3.19	4.34	9.07	760	$\bar{v}_{70} = 1.049$
10				2.00	3.74	5.46	11.24	760	
12				2.35	4.29	6.31	13.14	760	
14				2.77	4.88	7.27	14.96	760	
16				3.19	5.28	8.18	16.93	760	
18				3.47	5.86	9.08	18.94	760	
20				3.91	6.45	9.98	20.98	760	
								20	$\bar{v}_{40} = 0.450$
3	1.11	3.78	4.67	6.93	9.83			20	$\bar{v}_{45} = 1.00$
6	2.80	7.4	9.8	14.35	20.70			20	$\bar{v}_{50} = 1.60$
9	4.8	10.5	13.24	19.03	29.34			20	$\bar{v}_{55} = 2.00$
12	6.73	13		23.46	33.66			20	$\bar{v}_{60} = 3.00$
15	7.88	15.9		26.90					
18	8.72	18.3	25.80	29.78					
21	9.50	20.36	29.93	31.81					
24	10.14	22.07	33.11	33.34					
27	10.81	23.51	34.08						
30	11.18	24.80							
33	11.44	26.04							
36	11.82	27.16							
39	12.11	28.00							
42	12.21	28.81							
45	12.57	29.88							
48	12.80	31.00							
51	13.10	31.20							
54		32.50							
57		33.12							
60		33.62							
63		33.76							

SUMMARY

1. Heating curves have been determined for $CO(NH_2)_2$ and $CO(NH_2)_2 \cdot H_2O_2$ and the curve for the latter indicates the presence of a thermal effect at 64-67° associated with the decomposition of urea perhydrate.

2. Investigation of the decomposition of $CO(NH_2)_2 \cdot H_2O_2$ over the temperature range 40-70° and at pressures of 760 and 20 mm shows that increase in temperature and reduction in pressure have considerable effects on the process.

3. The compound $CO(NH_2)_2 \cdot H_2O_2$ is adequately stable below 20-30°.

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STUDY, WITH THE AID OF LABELED ATOMS, OF THE REACTION MECHANISM OF THE OXIDATION OF METHANE

MECHANISM OF THE FORMATION OF CARBON MONOXIDE

I. N. Antonova, V. A. Kuzmin, R. I. Moshkina, A. B. Nalbandyan, M. B. Neiman, and G. I. Feklisov

In work on photochemical oxidation of methane sensitized by mercury atoms, Nalbandyan [1] showed that at high temperatures the main reaction products are formaldehyde, carbon monoxide, and carbon dioxide. It was concluded from an analysis of the kinetic curves for the accumulation of these products that a sequence of reactions occurs in which formaldehyde is formed from methane, carbon monoxide from formaldehyde, and carbon dioxide from carbon monoxide, i.e. the occurrence of the following sequence of reactions was proved:

$$CH_4 \xrightarrow{+O_2} CH_2O \xrightarrow{+O_2} CO \xrightarrow{+O_2} CO_2.$$

In view of the importance of these conclusions for the mechanism of the oxidation of methane, the need arose for their verification for the thermal oxidation of methane, for which purpose we applied the new kinetic method developed by Nieman[2] for the study of reaction mechanisms with the aid of labeled atoms.

The present paper gives the results of the investigation of the way in which carbon monoxide is formed. For this purpose a detailed study was made of the kinetics of the accumulation of formaldehyde and carbon monoxide in presence of a small amount of labeled formaldehyde $C^{14}H_2O$, which was added to the reaction mixture of methane and air. The regularities observed in the kinetics of the changes in the specific activities of the formaldehyde and carbon monoxide formed in the course of the reaction enabled us to solve the problem in favor of the formation of carbon monoxide from formaldehyde.

EXPERIMENTAL

Methane was oxidized with atmospheric oxygen. In order to obtain appreciable amounts of intermediate products, a small amount of nitrogen oxides was added to the reaction mixture. The experiments were carried out in a continuous-flow apparatus. The reaction mixture, which contained about 35% of methane, 60% of air, 0.1% NO, 0.5% of carbon monoxide, and 0.07% of labeled formaldehyde ($C^{14}H_2O$), was passed to the reactor, which had been heated to 670°. The labeled formaldehyde was prepared by the incomplete oxidation of labeled methanol over a silver catalyst. The methanol was synthesized from labeled carbon dioxide by the method described by Feklisov [3].

The carbon monoxide was added to the reaction mixture with the object of determining whether the specific activity curves of formaldehyde and carbon monoxide intersect at the point corresponding to the maxium activity of carbon monoxide β_{CO}. In accordance with the theory of this kinetic tracer method, the intersection of the kinetic specific-activity curves of formaldehyde and carbon monoxide at the maximum value of β_{CO} is an unequivocal proof of the occurrence, as a stage in the sequence, of the process

$$CH_2O \xrightarrow{+O_2} CO.$$

Addition of labeled formaldehyde to the reaction mixture was effected by passage of part of the air through a bubbler containing 10% formaldehyde having specific activity of 0.5 microcurie/mmole. In order to prevent the polymerization of the formaldehyde passing on, the tubes connecting the bubbler to the reactor were heated to 100-120°. In order to asorb the formaldehyde gas leaving the reactor, a large absorption tower was used in which water flowed downward over a filling of short glass tubes.

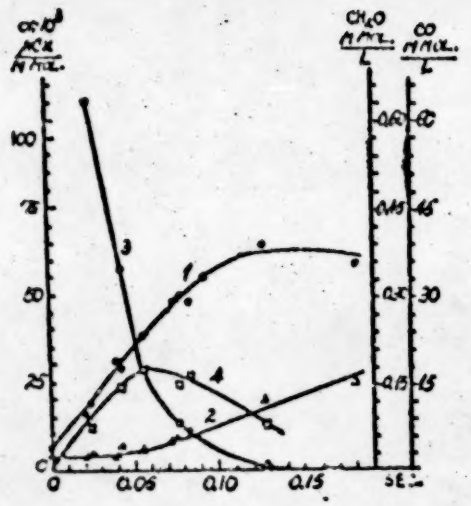

Fig. 1. Kinetics of the accumulation of formaldehyde (Curve 1) and carbon monoxide (curve 2) and the variation of their specific activities a_{CH_2O} (Curve 3) and β_{CO} (Curve 4)

After absorption of formaldehyde, the residual gas was collected in a gas holder. The formaldehyde content of the aqueous solution was determined by the hydroxylamine method. In order to obtain the solid precipitate necessary for the determination of the specific activity of the formaldehyde, it was converted into its 2,4-dinitrophenylhydrazone.

The amount of carbon monoxide and its specific activity were determined after oxidation with iodine pentoxide and absorption of the carbon dioxide formed in baryta water. The resulting precipitate of barium carbonate was centrifuged off, washed with hot water and with alcohol, dried, and weighed. Its specific activity was then determined.

Fig. 1 gives curves for the accumulation of formaldehyde (1) and carbon monoxide (2) as functions of the time spent by the reaction mixture in the reaction zone. It will be seen from Fig. 1 that the formaldehyde concentration increases as the time increases and attains a maximum for a time of 0.12-0.14 second. Further increase in the time results in a slow fall in the formaldehyde concentration. On the other hand, the carbon monoxide concentration rises continuously. The accumulation of carbon monoxide is characterized by the fact that, from the moment that formaldehyde ceases to accumulate, carbon monoxide begins to accumulate at a constant rate. The variations of the specific activities of formaldehyde (a_{CH_2O}) and carbon monoxide (β_{CO}) are represented by Curves 3 and 4 in Fig. 1. All the data and results for these experiments are given in Table 1.

It will be seen from 3 (Fig. 1) that the specific activity of formaldehyde diminishes with increase in time of contact, i. e. with increase in the formaldehyde content of the reacting mixture, whereas the specific activity of carbon monoxide (Curve 4) at first rises with time, and then begins to fall, more slowly, however, than the specific activity of formaldehyde. At the point corresponding to τ = 0.056 second the curves intersect and β_{CO} becomes equal to a_{CH_2O}.

As stated above, the intersection of the curves for the specific activities of formaldehyde and carbon monoxide in the point corresponding to maximum specific activity of CO is a direct proof of the sequence of processes:

$$CH_4 \longrightarrow CH_2O \xrightarrow{+O_2} CO.$$

An idea of the mechanism of the formation of carbon monoxide can be formed also from a comparison of the rate at which formaldehyde is consumed with the rate at which carbon monoxide is formed. If these rates are the same, then carbon monoxide must be formed by the oxidation or decomposition of formaldehyde. Let us denote the rate of formation of formaldehyde by w_{CH_2O} and the rate of its consumption by $k[CH_2O]$, then the rate of accumulation of formaldehyde $\frac{d[CH_2O]}{dt}$ can be written:

$$\frac{d[CH_2O]}{dt} = w_{CH_2O} - k[CH_2O],$$

so that the rate of consumption of formaldehyde is:

$$k[CH_2O] = w_{CH_2O} - \frac{d[CH_2O]}{dt} \qquad (1)$$

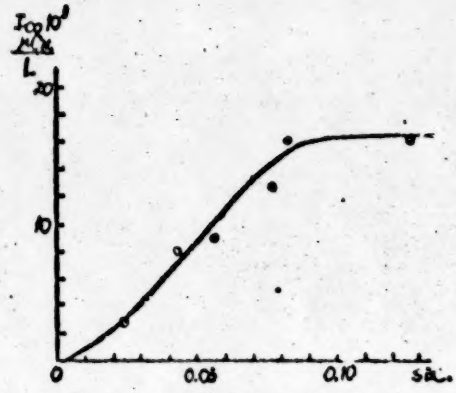

Fig. 2. Dependence of the activity of carbon monoxide on the time spent by the methane-air mixture in the reaction zone.

TABLE 2

Dependence of the Rates of Consumption of Formaldehyde and of Formation of Carbon Monoxide on the Time t spent by the Methane-Air Mixture in the Reaction Zone

t (seconds)	Rate of consumption of formaldehyde k [CH_2O]	Rate of formation of carbon monoxide w_{CO} (mmoles/liter · second)	
		according to Equation 2	calculated by graphical differentiation of the kinetic formation curves.
0.024	1.2	1.5	2.0
0.043	4.4	4.0	4.3
0.056	7.3	8.6	6.2
0.077	11.2	12.9	12.9
0.083	10.6	12.9	12.9

SUMMARY

1. A study was made of the kinetics of the oxidation of methane in presence of formaldehyde labeled with radioactive carbon.

2. It was shown by a kinetic method that, in the oxidation of methane, carbon monoxide is formed mainly from formaldehyde.

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PHYSICOCHEMICAL BASIS OF THE FORMATION OF DIFFUSIONAL SURFACE LAYERS ON IRON AND ITS ALLOYS

N. S. Gorbunov

The development of new industries and the continuous progress being made in technology demand the application of new, extremely strong and stable metals and alloys. In this connection the need arises for the protection of metal components and structures from corrosion and for the lengthening of their useful lives.

It is the external surface of these components, rather than layers below the surface, that is subjected to the most severe mechanical and corrosive action under conditions of use. In industry, therefore, methods of protecting the surface layer by hard-wearing and corrosion-resistant coverings – formed either by electrolysis or by diffusion – are widely adopted. When the diffusing elements are nitrogen or carbon, only the diffusion method of application is possible, since these elements do not form ions in solution. Diffusion methods, however, are used also for the surface application of metals that can be applied also by electrolysis.

Diffusional surface treatment with metals has an important advantage over electrolytic deposition, namely, that the bonding of the applied metal to the base metal is much stronger, owing to the formation of a diffusional intermediate layer between the base metal and the surface. Moreover, the gradual fall in the concentration of the metal through the depth of the diffusion layer is associated with a more gradual change in properties in the transition from the base metal to the surface.

By the application of different elements, it is possible to vary the properties of the surface layer of the treated metal within wide limits. For example, by the application of zinc or aluminum, the properties of the surface layers are improved with respect to the action of certain corrosive agents, whereas saturation of the surface with carbon results only in an improvement in mechanical properties. When, however, the surface of iron is saturated with nitrogen, chromium, silicon, or certain other elements, the surface layers are improved both with respect to mechanical properties, and also with respect to stability against the action of corrosive agents.

In diffusional treatments, either chemical compounds, or solid solutions, or both simultaneously may be formed in the surface layer of the metal. When a chemical compound is formed, the atoms of the applied element and of the metal-solvent combine together in definite proportions, and the solid phase consisting of this chemical compound can be denoted by a definite chemical formula. More frequently, however, the formation of continuous or limited solid solutions is observed in diffusional surface layers.

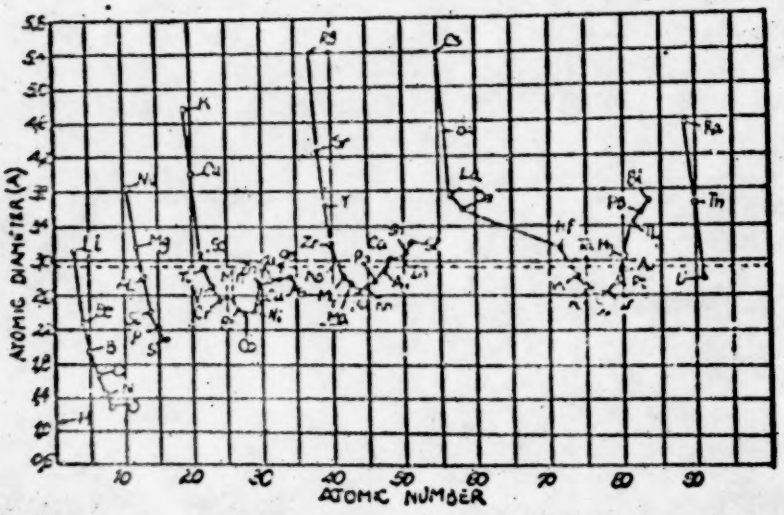
The work of Nikitin [1], Ageev [2], Kondlev [3], Grimm [4], Hume-Rothery [5], Kuznetsov [6], and other authors has indicated that the most important conditions affecting the formation of solid solutions are the dimensions and types of the crystalline lattices of the interdiffusing substances, and also the difference in atomic diameter. These same conditions apply also to the formation of diffusional surface layers.

Lyakishev and Portnova [7] established the existence of a definite relationship between the process of diffusional surface treatment and the conditions for the formation of chemical compounds and solid solutions between the metal to be treated and the substance applied.

However, in most papers on the process of diffusional metallization and the properties of the diffusional surface layers formed, no soundly based conclusions are stated regarding the possibility of the surface application of various substances to iron and its alloys. In the present investigation we sought to establish a relationship between the process of forming diffusional surface layers on iron and its alloys and the positions of the applied elements in Mendeleev's periodic system.

As already indicated, one of the main factors determining the possibility of forming solid solutions and diffusional surface layers is the difference between iron and the substance applied in atomic diameter. When the atomic diameter of the element diffusing into the metal to be covered is less than that of iron, or is greater, but not by more than 14-15%, distortion will occur in the crystal lattice of iron to an extent that will increase as the

difference in atomic diameter increases. When the diffusing atoms are 14-15% greater in diameter than those of the base metal, the crystal lattice of the metal-solvent will be deformed to its limit, and this difference in atomic diameters will therefore be a critical limit. In the diffusion of elements whose atomic diameters are more than 15% greater than the atomic diameter of the metal-solvent, the distortion in the crystal lattice of the latter will be so great that surface breakdown will occur. Hence, the relative values of the atomic diameters of the interacting elements evidently determine the possibility of forming solid solutions and of diffusional surface layers on the metal.



When we arrange the elements according to their atomic diameters and atomic numbers [8], we can establish the zone for solubility in iron and mark the boundary that will enable us to determine which elements can form diffusional surface layers on iron and its alloys. The atomic diameter of α-iron is 2.54 A, so that the upper limit of atomic diameter for elements capable of diffusing into iron will be 2.94 A.

In the figure we give data on the dependence of the atomic diameters of the elements on their atomic numbers. The upper limit of atomic diameter for elements that can form diffusional surface layers is indicated by a broken line. It must be assumed that elements below this line can give diffusional surface layers, but those that are above it cannot.

Apart from these dimensional relationships, for the formation of a diffusional surface layer it is essential also that the element applied should have a definite solubility in iron. Hence, the main factors determining the possibility of the formation of diffusional surface layers are 1) the type and parameters of the crystal lattices, 2) the values of the atomic diameters, 3) definite solubility of the applied element in iron.

EXPERIMENTAL

Our investigation of the formation of diffusional surface layers on iron and its alloys fully confirmed the existence of these fundamental physicochemical conditions for the formation of such diffusional layers. Results from the literature [8,9] and our own experimental results on the formation of surface layers on iron and its alloys are given below in tables. In the next to the last column, the value of the solubility of the element in iron (% by weight) is accompanied by an indication in parentheses of the temperature at which the solubility was determined. In the last column of the table it is stated whether or not the given element forms a diffusional surface layer.

The diffusional surface treatment, except in the cases indicated by an asterisk, was carried out in the Dispersed System Section of the Institute of Physical Chemistry of the USSR Academy of Sciences, which is under the directorship of P. A. Rebinder. The diffusional treatment of surfaces of iron and iron alloys was carried out by various methods, and the processes were performed in various atmospheres: a hydrogen reducing atmosphere, a mixture of hydrogen and hydrogen chloride, an atmosphere of gaseous chlorine, and also a vacuum in the case of a new method of diffusional metallization that we have developed. The starting materials for the application of the coverings were pure metal powders, or, in rare cases, alloys of the metals with iron.

In the tables the results on the diffusional surface treatment of iron and its alloys are arranged according to the groups and subgroups in Mendeleev's periodic system.

The data in Table 1 show that elements of Subgroup A do not form diffusional surface layers. Of the elements of Subgroup B, copper and gold form such layers, but silver does not on account of its lack of solubility in iron.

Of the metals of Group II, only beryllium and zinc give diffusional surface layers, whereas the remaining metals do not, since they are insouble in iron and the difference in atomic diameter exceeds 15%.

TABLE 1

Diffusional Surface Layers Formed by Elements of Group I of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at		Diffusional surface layer
			room temperature	high temperature	
Subgroup A					
Lithium	3.13	23	0	0	Not formed
Sodium	3.83	50	0	0	"
Potassium	4.76	87	0	0	"
Rubidium	5.40	116	0	0	"
Cesium	5.40	116	0	0	"
Subgroup B					
Copper	2.55	1	0.35	8.0 (1084)	Formed
Silver	2.88	13	0	0	Not formed
Gold	2.87	13	0.6	15.0 (1170)	Formed

TABLE 2

Diffusional Surface Layers Formed by Elements of Group II of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at		Diffusional surface layer
			room temperature	high temperature	
Subgroup A					
Beryllium	2.25	−11	4.5	6.0 (1150)	Formed [10]
Magnesium	3.20	25	0	0	Not formed
Calcium	3.93	55	0	0	"
Strontium	4.29	69	0	0	"
Barium	4.48	76	0	0	"
Subgroup B					
Zinc	2.74	9	6.0	Unknown	Formed
Cadmium	3.04	20	0	0	Not formed
Mercury	3.10	22	0	0	"

Of the elements of Group III, boron and aluminum form diffusional surface layers and thallium does not; there are no available data for the remaining elements of this group.

Of the elements of Group IV, titanium, carbon, and silicon form diffusional surface layers and lead does not; there are no data for the remaining elements.

Metals of Group V, Subgroup A, have cubic body-centered crystal lattices, like iron, and they do not differ from iron by more than 15% in atomic diameter. Moreover, they are fairly soluble in iron, particularly at high

TABLE 3

Diffusional Surface Layers Formed by Elements of Group III of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at room temperature	Solubility of element in iron at high temperature	Diffusional surface layer
		Subgroup A			
Boron	1.94	−24	0.06	0.18 (1174)	Formed
Aluminum	2.80	10	32.0	35.0 (1232)	"
Scandium	3.02	19	Unknown	Unknown	—
Yttrium	3.62	40	"	"	—
		Subgroup B			
Gallium	2.74	9	Unknown	Unknown	—
Indium	2.13	−23	"	"	—
Thallium	3.43	35	0	0	Not formed

TABLE 4

Diffusional Surface Layers Formed by Elements of Group IV of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at room temperature	Solubility of element in iron at high temperature	Diffusional surface layer
		Subgroup A			
Titanium	2.93	15	3.0	6.0 (1295)	Formed
Zirconium	3.19	25	0.15	Unknown	—
Hafnium	3.17	25	Unknown	"	—
		Subgroup B			
Carbon	1.54	−40	0.02	1.7 (1145)	Formed
Silicon	2.34	−8	13.0	18.5 (1195)	"
Germanium	2.78	10	Unknown	Unknown	"
Tin	3.16	23	8.0	16.0 (1110)	—
Lead	3.49	37	0	0	Not formed

TABLE 5

Diffusional Surface Layers Formed by Elements of Group V of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at room temperature	Solubility of element in iron at high temperature	Diffusional surface layer
		Subgroup A			
Vanadium	2.69	6	100	100	Formed
Niobium	2.94	15	0.5	12.0 (1350)	"
Tantalum	2.94	15	0.17	6.5	"
		Subgroup B			
Nitrogen	1.42	−41	0.015	Unknown	Formed [11]
Phosphorus	2.20	−13	1.0	2.8 (1050)	—
Arsenic	2.80	10	5.0	7.0 (830)	Formed
Antimony	3.23	27	7.0	8.0 (998)	Not formed
Bismuth	3.64	43	0	0	"

TABLE 6

Diffusional Surface Layers Formed by Elements of Group VI of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at room temperature	Solubility of element in iron at high temperature	Diffusional surface layer
		Subgroup A			
Chromium	2.57	1.5	100	100	Formed
Molybdenum	2.80	10	5.0	34.0 (1440)	"
Tungsten	2.92	11	8.0	33.0 (1525)	"

TABLE 7

Diffusional Surface Layers Formed by Elements of Group VII of the Periodic System

Element	Atomic diameter (A)	Difference in atomic diameter (%)	Solubility of element in iron at room temperature	Solubility of element in iron at high temperature	Diffusional surface layer
		Subgroup A			
Manganese	2.60	2	100	100	Formed
Technetium	—	—	—	—	—
Rhenium	2.75	8.2	29.0	Unknown	—

temperatures. Consequently, they all form diffusional surface layers. Of the elements of Group V, Subgroup B, nitrogen and arsenic form diffusional surface layers, but antimony and bismuth do not. Of the elements of Groups VI and VII, the metals of the A subgroups are of interest.

All metals of Group VI, Subgroup A, form diffusional surface layers, the data for these metals being similar to those for metals of Group V, Subgroup A.

Of the metals of Group VII, Subgroup A, manganese forms diffusional surface layers, but there are no data for technetium and rhenium.

Hence, an examination of the process of the formation of diffusional surface layers on iron and its alloys by the elements, as arranged in the groups and subgroups of Mendeleev's system, leads to the conclusion that the tendency for this process to occur depends on the structures and parameters of the crystal lattices of iron and of the applied element, on the difference in atomic diameter between iron and the applied element, and on the solubility of the applied element in iron in the solid state at ordinary and elevated temperatures. We consider that these conclusions regarding the diffusional surface treatment of iron and its alloys can be applied also to the similar treatment of other metals and complex alloys.

In conclusion the author wishes to express his great indebtedness to Dr. V. I. Likhtman for valuable discussions.

SUMMARY

1. The principal physicochemical conditions for the formation of diffusional surface layers on iron and its alloys are stated.

2. Diffusional layers are formed at the surface of the base metal as a result of the penetration of the applied substance into the crystal lattice of the metal-solvent.

3. The main physicochemical conditions determining the possibility of the formation of diffusional surface layers are: similarity in type between the crystal lattices of the applied element and of iron, a diffusing element of smaller atomic diameter than iron (if it is greater, then the difference in atomic diameter must not be more than 15%), and, finally, adequate solubility of the applied element in iron at ordinary and elevated temperatures.

4. These fundamental physicochemical conditions for the formation of diffusional surface layers are quite general and can be applied to the diffusional surface treatment of other metals and alloys.

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DETERMINATION OF THE CRYSTALLIZATION COEFFICIENT FOR THE DISTRIBUTION OF A THORIUM B (RADIOACTIVE LEAD) SALT BETWEEN A SALT MELT AND CRYSTALS OF AN ISOMORPHOUS SALT

V. R. Klokman, V. K. Zinovyeva, and I. A. Tseveleva

Experimental investigations [1], carried out by one of us in collaboration with Khlopin, on the distribution of a micro component between a melt and a solid phase isomorphous with the micro component were confined to the distribution of radium between a melt and the crystals of a salt isomorphous with the corresponding radium salt. These investigations showed that in all of the systems studied the crystallization coefficient of radium for distribution between melt and an isomorphous salt at 300-600° was always less than its crystallization coefficient for distribution between a solution and the same isomorphous salt; the numerical value of the crystallization coefficient was never greater than unity. This indicates the absence of enrichment of the isomorphous solid phase with radium during crystallization from the melt.

Khlopin, Klokman, Murin, and Nefedov [2], in a study of the mechanism of the attainment of equilibrium with respect to the micro component during the separation of the solid phase from the melt, showed that, in the melt, as in the solution equilibrium distribution of radium occurred by a process of recrystallization. However, in the melt at relatively high temperatures the process is much more rapid. The equilibrium value of the crystallization coefficient of radium in the recrystallization of excess of barium nitrate in a melt of constant composition was attained in four hours at 315° and in one hour at 465°. The present investigation had the object of verifying these peculiarities in behavior for another micro component, namely, the radioactive isotope of lead ThB.

A study of the distribution of the radioactive isotope of lead RaD between solution and crystals of barium chloride and of barium nitrate at various temperatures was made by Polesitsky, who obtained the following values for the crystallization coefficients D: In the system $BaCl_2$ – $RaDCl_2$ – H_2O $D_{100°} = 1.32$, and in the system $Ba(NO_3)_2$ – $RaD(NO_3)_2$ – H_2O $D_{0°} = 0.16$ [3]. In the first case the solid phase was enriched in radioactive lead, even at 100°, and in the second case the liquid phase was enriched in micro component, even at 0°, and the crystallization coefficient was less than unity.

If the peculiarity that we have noticed – the non-enrichment of the isomorphous solid phase in micro component during crystallization from a melt – is a normal characteristic of the phenomenon, then for the distribution of ThB between melt and crystals of barium chloride the crystallization coefficient D should be less than or equal to unity, and for the distribution of ThB between melt and crystals of barium nitrate the crystallization coefficient D should be considerably less than unity. We were interested also in verifying, for another system, the time required for the establishment of equilibrium in the distribution of the micro component between the melt and crystals of an isomorphous salt. We determined the crystallization coefficients of ThB for the binary systems $Ba(NO_3)_2$ – $BaCl_2$ and $Ba(NO_3)_2$ – $NaNO_3$. The rate at which equilibrium with respect to the micro component was established was studied for the system $BaCl_2$ – $Ba(NO_3)_2$.

EXPERIMENTAL

Recrystallized, carefully dried barium chloride, barium nitrate, and sodium nitrate were used in the experiments. The temperature of the melts was measured with a thermocouple of platinum and platinum-rhodium, which was graduated without its pocket against the temperatures at which the crystallization of various salts begins. The experiments were carried out in porcelain crucibles. The melt was stirred with a quartz stirrer.

The radioactive isotope of lead ThB was prepared in the usual way by collecting the active deposit produced by thoron on a negatively charged platinum plate. The active deposit from thoron was then removed from the plate by boiling it for a few minutes in 0.1 N HNO_3 containing a small fraction of a milligram of lead nitrate. The active solution so obtained was evaporated in the crucible in which the experiment was to be performed. The inactive lead was added to reduce adsorption on the crucible walls and stirrer during the experiment.

The experimental procedure for the determination of the crystallization coefficient of ThB did not differ in principle from that which we used for similar determinations on radium [1]. The only difference was that, instead of the special pipets that we used previously for taking melt samples, in this work samples of the initial melt were taken with simple glass tubes (diameter 8 mm) and test samples of the final melt were taken with tubes whose end were drawn out to form capillaries. Two duplicate test samples were taken on each occasion.

The cooled samples of melt were extracted from the tubes and dissolved in hot 0.1 N HNO_3. Lead nitrate (5 mg) was added to each solution, and was then precipitated by hydrogen sulfide in weakly ammoniacal solution. On the next day the lead sulfide was filtered off onto a small piece of retentive filter paper, which was laid on an aluminum dish having a perforated bottom. The dish was placed on a special test tube having a wide flat rim, which was previously greased so that the dish made close contact with the test tube. The test tube was provided with a side tube, which was attached to a water pump. The precipitates were dried in a drying cupboard at 60-70°, and their activities were then measured with a β-counter. The mean error of the activity measurements was $\pm$ 2%.

Determination of the Crystallization Coefficient for the Distribution of ThB between the Melt and Barium Chloride Crystals in the System $BaCl_2 - Ba(NO_3)_2$. According to the literature [4], the system $BaCl_2 - Ba(NO_3)_2$ is a simple binary system having a eutectic point at 497° and 37.3 mole % of barium chloride. On the fusion curve that we determined, the eutectic was found to be at 503° at a composition of 37.3 mole % of barium chloride, which is in quite satisfactory agreement with the reported data.

We determined the amount of ThB passing into the solid phase by measuring the activity of the melt before and after the separation of various amounts of barium chloride. The separation of solid phase from the saturated melt was carried out by the gradual lowering of the temperature of the original melt to the crystallization temperature of the previously selected final melt. The final melt was the same in all experiments (40 mole % of barium chloride, i.e. 8 g of $Ba(NO_3)_2$ and 4.285 g of $BaCl_2$; crystallization temperature 525°). The amount of solid phase separating was 0.4-1.4 g of $BaCl_2$, i.e. 2.9-11.5% of the total amount of barium ions in the melt (both ions derived from barium chloride and also ions derived from barium nitrate).

TABLE 1

Expt. No.	Amount separating into the solid phase		D
	Ba (%)	ThB (%)	
1	2.9	2.1	0.72
2	3.9	3.0	0.77
3	5.2	4.5	0.86
4	7.3	6.4	0.87
5	8.0	6.5	0.80
6	8.3	7.1	0.85
7	9.1	7.5	0.81
8	11.5	9.0	0.76
		Mean	0.80 $\pm$ 5%

The crystallization coefficient D was calculated from the formula:

$$D = \frac{x(100-y)}{y(100-x)},$$

in which x and y are the percentages of micro and macro component, respectively, passing into the solid phase, and $(100-x)$ and $(100-y)$ are the percentages of micro and macro component remaining in the melt. The results of the experiments on the determination of the crystallization coefficients for the distribution of ThB between the melt and barium chloride crystals are given in Table 1.

It will be from these results that the crystallization coefficient D remains constant within $\pm$ 5% for a 3.5-fold variation in the amount of solid phase separated. It was found, as expected, that the crystallization coefficient of ThB in this system is less than unity, so that in this case no enrichment of the solid phase in micro component occurs.

Determination of the Crystallization Coefficient for the Distribution of ThB between the Melt and Barium Nitrate Crystals in the Binary Systems $Ba(NO_3)_2$ and $Ba(NO_3)_2 - NaNO_3$ and $Ba(NO_3)_2 - BaCl_2$. The fusion curve that we determined for the binary system $Ba(NO_3)_2 - NaNO_3$ had a eutectic point at 296° and 11.6 mole % of $Ba(NO_3)_2$, which is in close agreement with the results of Harkins and Clark [5] [296° and 11.0 mole % of $Ba(NO_3)_2$] and with our own results [1] [297° and 11.1 mole % of $Ba(NO_3)_2$].

In the determination of the crystallization coefficient of ThB in this system we used two methods for the determination of the amount of ThB passing into the solid phase. On the one hand we determined the activity of the melt before and after the separation of the solid phase, and on the other hand we determined the activity of the solid phase itself. In the latter case, after the separation of the barium nitrate precipitate, the whole of the melt was drawn off as far as possible. The residue was washed from the crucible with 0.1 N HNO_3, and its activity was

measured after precipitation as lead sulfide. The activity of interest to us – the activity of the $Ba(NO_3)_2$ precipitate – was determined as the difference between the activity of the whole residue and that of the remaining melt. In the calculation, the activity desorbed from the crucible walls during treatment of the residue with an acid solution was taken into account.

As we considered that in this system the crystallization coefficient D should be very small, the maximum possible amount of barium nitrate – about 60-75% – was separated into the solid phase. The absolute amount of barium nitrate which passed into the solid phase was about 5 g. The composition of the final melt was 16.8 mole % of $Ba(NO_3)_2$, and the temperature at which its crystallization began was 320°. The results of the experiments are given in Table 2.

TABLE 2

Expt. No.	Amount separating into the solid phase			D, calculated from the activity of the melt	D, calculated from the activity of the precipitate
	$Ba(NO_3)_2$ (%)	ThB			
		according to melt (%)	according to precipitate (%)		
1	60	4.7	8.2	0.03	0.06
2	75	16.0	16.0	0.06	0.06
3	75	4.0	11.1	0.01	0.04
4	75	9.9	5.6	0.04	0.02
5	75	22.8	21.3	0.09	0.09
			Mean	0.05 ± 0.02	0.05 ± 0.02

TABLE 3

Experiment No.	Time of crystallization	Amount of		D
		Ba separating into the solid phase (%)	ThB separating into the solid phase (%)	
1	15 minutes	8.8	1.0	0.10
2	30 minutes	9.1	4.9	0.51
3	45 minutes	9.2	5.6	0.59
4	1 hour	9.1	7.1	0.78
5	1 hour 15 minutes	9.2	7.9	0.85
6	1 hour 30 minutes	9.2	7.8	0.83

As can be seen from Table 2, our experimental results show that ThB is indeed not greatly entrained by the separating barium nitrate crystals. As regards the absolute value of the crystallization coefficient, we can say only that it is probably considerably less than unity, for, although the mean values of the crystallization coefficient obtained in two different ways are identical, the fluctuation in the values obtained in each series of experiments, even for the separation of a given amount of solid phase, are so great (about 50%) that we cannot say for certain whether or not we are dealing here solely with isomorphous cocrystallization. It is probable that in this system, which is made up entirely of nitrates, partial decomposition of lead nitrate occurs and is followed by adsorption of decomposition products on the surface of barium nitrate crystals. In order to verify this hypothesis we determined the crystallization coefficient for the distribution of ThB between the melt and barium nitrate crystals in another system – $Ba(NO_3)_2 - BaCl_2$ – in which we had already determined the crystallization coefficient for the distribution of ThB between the melt and barium chloride crystals and obtained agreeing results.

Three experiments were carried out on this system. In these experiments, 33%, 52%, and 67% of the total amount of barium ions were separated as solid phase. The experiments were carried out at 520°. In all cases, even when 67% of the barium ions was separated into the solid phase, no entrainment of ThB by the crystals could be detected. These results confirm our supposition that in the crystallization of the solid phase from the melt, either there will be no isomorphous coprecipitation at all of ThB with barium nitrate crystals, or the crystallization coefficient of ThB will be so small in this case, that, with the accuracy with which we can measure the activities of the initial and final melts, we shall not be able to detect the entrainment of ThB by the solid phase. Moreover, these results indicate also that no decomposition of lead nitrate occurs in the system $Ba(NO_3)_2 - BaCl_2$ in spite of the higher temperature of the experiment.

Determination of the Rate of Attainment of Equilibrium for the Distribution of ThB between Melt and Crystals of Barium Chloride. In order to determine the rate of attainment of equilibrium with respect to the micro component in the distribution of ThB between melt and crystals of barium chloride, we carried out the recrystallization of a given amount (0.8 g) of barium chloride (finely ground and passed through a cambric sieve) in a melt of constant composition (40 mole % of $BaCl_2$) at constant temperature (525°) for various intervals of time. The time of recrystallization was varied from 15 to 90 minutes. The amount of ThB passing into the solid phase was determined from the difference in the activity of the melt, before and after the recrystallization of the solid phase in it. The results of the experiments are given in Table 3.

As can be seen from Table 3, as the time of recrystallization was increased, the value of the crystallization coefficient approached more and more closely to its equilibrium value, and, within the limits of experimental error, the equilibrium of D was attained already after one hour. These results are in accord with our previous results on the attainment of equilibrium in the distribution of radium between melt and crystals of barium nitrate [2]. In this case also, the equilibrium value of the crystallization coefficient of radium was attained in one hour at 465°.

In conclusion, we wish to thank Prof. A. P. Ratner for valuable discussions.

SUMMARY

1. The crystallization coefficient for the distribution of ThB between a salt melt and barium chloride crystals was determined (D = 0.80).

2. It was shown that the crystallization coefficient for the distribution of ThB between a salt melt and barium nitrate crystals is much less than unity.

3. It was established that in the distribution of the radioactive isotope of lead ThB between salt melts and crystals of isomorphous salts, no enrichment of the solid phase in the micro component occurs.

4. It was shown that, at about 500°, a state of equilibrium in the distribution of ThB between a melt and an isomorphous solid phase is established in one hour.

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ROLE OF DISSOCIATIONAL ACTIVATION IN THE SINTERING OF OXIDES OF ELEMENTS OF VARIABLE VALENCY

A. I. Leonov

It is known that the sintering occurring during the firing of ceramics and refractories is affected by the surrounding atmosphere of gases. The effect of the atmosphere is most marked for oxides of elements of variable valency. In order to determine the mechanism by which the atmosphere affects the sintering of oxides, we have carried out expriments on the sintering of copper, iron, and magnese oxides.

EXPERIMENTAL

Copper carbonate, manganese carbonate, and iron oxalate were converted into the corresponding oxides by calcination at 600° for one hour. The oxides were compressed into rectangular bars 30 x 7 x 3 mm, under a pressure of 500 kg/sq.cm. The length of the sample was measured before and after the experiment, and the linear shrinkage was calculated. The samples were heated in a hermetically closed tube furnace. Evacuation was carried out by means of a rotary pump. Some of the experiments were carried out in argon.

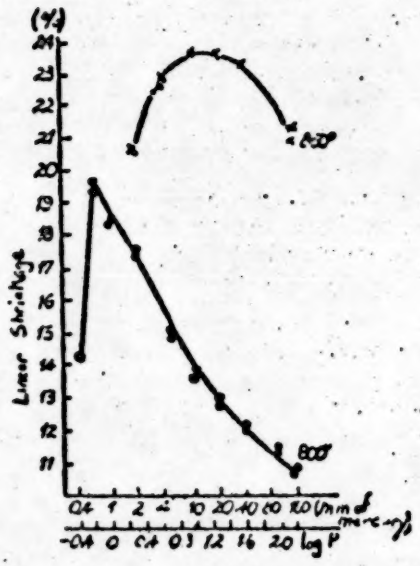

Fig. 1. Effect of oxygen pressure on the linear shrinkage of cupric oxide during firing. Duration of treatment at temperatures indicated, one hour

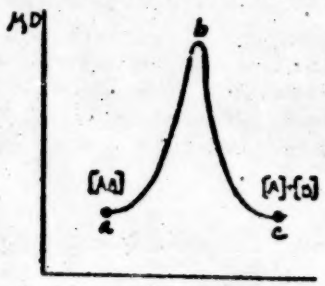

Fig. 2. Scheme of dissociational activation.

The sintering of cupric oxide was carried out at 800° and at 850°, the time of treatment being one hour. The results are shown in Fig. 1, in which the oxygen pressure (log p) at which the firing is carried out is plotted as abscissa. The oxygen pressure was taken to be 0.21 times the pressure of the air. The ordinates are values of the percentage linear shrinkage of the samples after a one-hour treatment.

As can be seen from Fig. 1, the linear shrinkage of a cupric oxide sample depends on the pressure of oxygen in the furnace. When sintering is carried out at 800°, diminution in the pressure of oxygen in the furnace is accompanied by increased linear shrinkage, which attains a maximum at about 0.5-1 mm of mercury; with further reduction in oxygen pressure, the shrinkage diminishes sharply. At 850° maximum sintering occurs at 10-20 mm of mercury. According to the literature [1], the dissociation pressure of cupric oxide ($2CuO \rightleftharpoons Cu_2O + 0.5O_2$) is about 1 mm at 900° and 10-15 mm at 850°. It will be seen that maximum shrinkage occurs when the oxygen pressure in the gas phase is equal to the dissociation pressure of cupric oxide. The shrinkage decreases both at higher and at lower oxygen pressures in the furnace.

We explain the observed effect of oxygen pressure on the sintering of cupric oxide by the occurence of dissociational activation. The concept of dissociational activation is based on the view that in the dissociation and association of a substance the molecules pass through an activated transition state. In this transition state the molecules have a higher rate of diffusion and higher chemical activity than molecules in the stable state. Such a process is represented diagrammatically in Fig. 2, in which D is the coefficient of diffusion, μ is the chemical activity, [AB], [A], and [B] represent stable states of the molecules, and the curve abc represents the variation of the coefficient of diffusion and chemical activity of molecules in the transition state.

The greater the number of reversible changes (dissociation $\rightleftharpoons$ association) undergone by each molecule of a substance in unit time, the more vigorously will chemical and physical processes take place in this substance (chemical reactions, crystallization, sintering). The kinetics of such processes, therefore, depend on the degree of dissociation of the substance, which can be calculated from the free energy of formation of the compound, or determined by measuring the dissociation pressure of the oxide. The degree of dissociation of an oxide can be varied by change in temperature or by change in the pressure of oxygen in the gas phase.

The effect of oxygen pressure on the degree of dissociation of cupric oxide can be ascertained with the aid of the mass-action law, which for the dissociation reaction AB $\rightleftharpoons$ A + B can be expressed by the equation:

$$\frac{[A][B]}{[AB]} = K,$$

in which [AB] is the concentration of the substance AB, [A] and [B] are the concentrations of the dissociation products, and K is the equilibrium constant.

If we increase the concentration of, for example, B by adding an extra amount of this to the system then since K is a constant, [A] will diminish and [AB] will increase, i. e. addition of one of the dissociation products will lower the degree of dissociation. The dissociation pressure of cupric oxide at 800° is 1 mm [1], and the partial pressure of oxygen in the air under normal conditions is about 160 mm, i. e. is 160 times as great as the dissociation pressure of cupric oxide. If the oxygen pressure in the furnace is lowered, then, in accordance with the mass-action law, the degree of dissociation of cupric oxide will increase. Under these conditions the rate of diffusion and reactivity of cupric oxide should increase, and such an increase was observed in our experiments. When the oxygen pressure in the gas phase falls below the equilibrium value, all the cupric oxide is reduced to cuprous oxide and the extent of dissociational activation falls sharply, the dissociation pressure of cuprous oxide being very low (about 10^{-6} mm) at 800° [1].

It will be obvious that each cupric oxide molecule will undergo the greatest number of acts of dissociation in unit time when the pressure of oxygen in the gas phase is equal to the dissociation pressure of the oxide. Under these conditions, the rate of diffusion and the reactivity of oxide molecules are at a maximum, and all kinetic processes in cupric oxide proceed at their maximum rates.

Experiments on the sintering of iron and manganese oxides again showed that the linear shrinkage is dependent on the pressure of oxygen in the furnace. For example, when the oxides were treated at 1000° for one hour and the furnace contained air at 760 mm, the linear shrinkages were 20% for ferric oxide and 21.5% for manganic oxide, but in treatments for the same time and at the same temperature at a residual pressure of 2 mm or in an atmosphere of argon (760 mm) the linear shrinkages rose to 24% for ferric oxide and 24.8% for manganic oxide.

The dissociation pressure of Fe_2O_3 at 1000° is 0.3 mm [2], and the partial pressure of oxygen in the air is 160 mm, i. e. is 533 times as high as the dissociation pressure of Fe_2O_3. In these experiments, as in those with cupric oxide, reduction of the oxygen pressure in the furnace increases the degree of dissociation of ferric oxide, with the result that activation of sintering occurs. The same is true of manganic oxide.

Analogous results were obtained by Bukhikov and Tresvyatsky [3] in a study of the effect of the gaseous medium on the tendency of chromic oxide to sinter. Their experiments showed the sintering of Cr_2O_3 is poor when it is fired in an oxidizing medium. If, however, the chromic oxide if fired in absence of oxygen — for example, in argon, in nitrogen, or in a vacuum — it sinters very readily, forming a compact crystalline material. The results of the experiments are given in the table.

On the basis of these experiments, Bukhikov and Tresvyatsky suggested that the cause of the poor sintering of chromic oxide in an oxidizing medium is the partial surface oxidation of the oxide with formation of hexavalent chromium ions. When the firing is carried out in a neutral gaseous medium, oxidation of the chromic oxide does

TABLE

Effect of the Gaseous Medium on the Sintering of Pure Chromic Oxide during Firing

Firing conditions	Firing temperature (°C)		
	1400	1500	1600
	True porosity (%)		
Firing in an oxidizing medium in a flame furnace	49.36	48.96	39.83
Firing in a vacuum furnace at a residual pressure of 1-3 mm	46.38	13.61	11.46
Firing in a neutral gas (nitrogen)	45.89	16.31	10.50

not occur and its sintering proceeds normally. According to our views, the cause of the satisfactory sintering of chromic oxide in a vacuum or in nitrogen, as compared with an oxidizing medium, lies in the following facts. The calculated dissociation pressure of Cr_2O_3 [2] at 2000° is 3mm, and at 3000° 760 mm. At 1400-1600° it will be in the region of 0.1-0.01 mm. Under a reduced pressure of 1-3 mm or in an inert gas the oxygen pressure will be about one-hundredth of its value in an oxidizing medium (100 mm), so that in a vacuum or in nitrogen the degree of dissociation of Cr_2O_3 is higher and the processes of diffusion and sintering of Cr_2O_3 proceed more rapidly.

It will be evident from the above considerations that dissociational activation plays an important part in the sintering of oxides of elements of variable valency (Fe_2O_3, Cr_2O_3, Mn_2O_3, TiO_2, SnO_2, CuO, CoO, etc.). The phenomenon of dissociational activation must be taken into account in the technology of the manufacture and in the use of refractories (chromomagnesite, chromites, etc.), and in the manufacture of special ceramics (ferrites, titanates, stannates).

SUMMARY

1. The effect of the pressure of oxygen in the gaseous medium on the sintering of oxides of elements of variable valency is demonstrated.

2. The theory of dissociational activation is expounded. It provides an explanation of the mechanism of the action of oxygen on the chemical and physical processes occurring in oxides during firing.

3. The importance of the effect of dissociational activation on the synthesis and use of materials prepared from oxides of elements of variable valency is pointed out.

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REACTION OF ALKYL 2-CHLOROVINYL KETONES WITH ETHYL ACETOACETATE

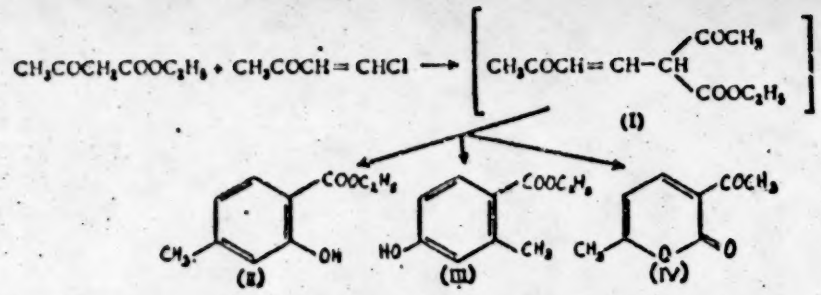
N. K. Kochetkov, L. I. Kudryashov, and A. N. Nesmeyanov

2-Chlorovinyl ketones are capable of undergoing a great variety of reactions, and various aliphatic, alicyclic, and heterocyclic compounds can be prepared by their aid [1]. However, the reaction of 2-chlorovinyl ketones with compounds containing an active methylene group, such as ethyl acetoacetate, has not been investigated. It is known that 3-(chloromethylene)camphor – which may be considered to belong, formally, to the class of 2-chlorovinyl ketones, although it differs considerably in chemical behavior from simple alkyl 2-chlorovinyl ketones – reacts with ethyl sodioacetoacetate in alcoholic solution with formation of ethyl Δ^{3}-β-camphorpropionate [2]. This reaction is thus associated with simultaneous alcoholysis of an acetyl group. It was found that the same reaction carried out in an inert medium proceeds in a complex fashion, and no definite results were obtained [2]. Attempts have been made to effect the condensation of 2-chlorovinyl phenyl ketone with sodioacetoacetic and sodiomalonic esters in benzene, but again no positive results were obtained [3]

We have studied the reaction, under various conditions, of ethyl acetoacetate with 2-chlorovinyl methyl ketone. The reaction of ethyl sodioacetoacetate with 2-chlorovinyl methyl ketone in benzene did not give unequivocal results: the product obtained was a complex mixture formed as the result of obscure secondary reactions. Negative results were obtained also in the condensation of ethyl acetoacetate with 2-chlorovinyl methyl ketone in aqueous alkaline medium, in diethylaniline, and in presence of caustic potash in benzene. The use of acid condensing agents – zinc chloride and acetic anhydride – was also unsuccessful. A positive result was obtained in the reaction of 2-chlorovinyl methyl ketone only in presence of calcined potassium carbonate in benzene, toluene, or xylene. As yet, potassium carbonate is the only suitable condensing agent found. The reaction mixture, after the usual treatment, yielded ethyl 4-methylsalicylate. This was not the only substance formed in the condensation process, for a substance melting at 61° was also isolated, and preliminary investigation showed that this is a substance formed from the "bisketovinylated" • product and is probably a benzofuran derivative. The yield of substituted salicylic ester is increased by the use of excess of ethyl acetoacetate. Thus, when equimolecular amounts of reactants are used the yield is 10%, when a two-fold excess of ethyl acetoacetate is used the yield is 16%, for a five-fold excess it is 32%, and for a ten-fold excess it is 40%. The temperature also has some effect: in boiling benzene (five-fold excess of ethyl acetoacetate) the yield of the salicylic ester is 28%, in boiling toluene it is 32%, and in boiling xylene it is 34%. Higher-boiling solvents cannot be used because 2-chlorovinyl methyl ketone resinifies completely above 140-150°. The formation of a substituted salicylic ester as a result of this reaction can be represented as follows. 2-Chlorovinyl methyl ketone reacts with ethyl acetoacetate with formation of the normal "monoketovinylated" product (I) by reaction at the methylene group. We shall not consider the question of whether (I) is formed by direct ketovinylation at carbon, by migration of a ketovinyl group from oxygen in the original O-ketovinylated product, or by Michael condensation with subsequent dehydrohalogenation. This question requires special investigation, but it is obvious that initially an intermediate product of type (I) must be formed. The ketovinylation product (I) is able to undergo further reactions. It is particularly necessary to note that the hydrogen on the central carbon atom, being under the influence of three carbonyl groups, is highly mobile, so that the entry of a second ketovinyl group is greatly facilitated. The importance for the result of the reaction of an excess of ethyl acetoacetate now becomes understandable; this excess will naturally reduce the possibility of the second ketovinylation and the formation of reaction products of greater complexity. The cause of the lack of success in the condensation of a chlorovinyl ketone with ethyl sodioacetoacetate is also clear: the transmetallization of the monoketovinylation product by ethyl sodioacetoacetate will readily occur, and can be followed by a second substitution reaction.

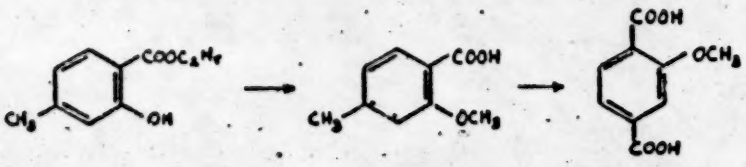
• Under suitable reaction conditions the intermediate product (I) can also undergo cyclization; and in our case cyclization is, in fact, found to occur. It can occur in various ways, and of these we must consider three – formation of the 4-methylsalicylic ester (II), of its isomer (III), and of the 2H-pyran-2-one derivative (IV):

• We shall refer to the introduction of a ketovinyl group RCOCH=CH– into the molecule of an organic compound – which is usually effected by the action of a 2-chlorovinyl ketone – as "ketovinylation".

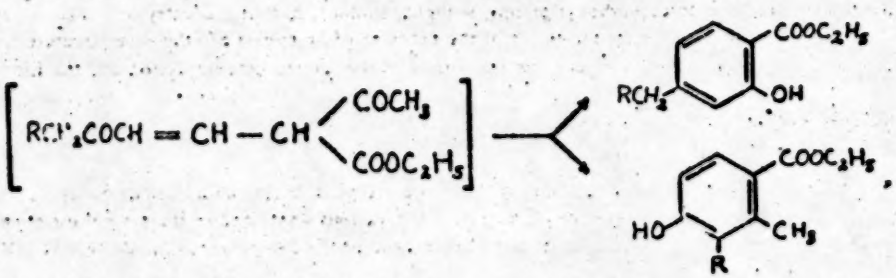


As regards the last compound (IV) we cannot assert that it is not formed in the reaction, since the by-products of the reaction included small amounts of substances whose structures were not established.

Our main attention, however, was given to the isolation of a hydroxytoluic ester, which was the main reaction product and was obtained, under optimum conditions, in yields of up to 40%. The choice between the two possible structures for this substance – (II) and (III) – was made on the basis of the following data. In aqueous solution the substance gave a color with ferric chloride, which is characteristic for salicylic acid derivatives; p-hydroxybenzoic acid derivatives do not give this reaction. Hydrolysis of the substance gave a crystalline acid that corresponded in properties to 4-methylsalicylic acid and could be decarboxylated to m-cresol. Final proof of the structure of the condensation product as a 4-methylsalicylic ester (II) was provided by its methylation with dimethyl sulfate followed by oxidation of the methylation product, which was not isolated in the pure form. The only reaction product obtained was methoxyterephthalic acid, the formation of which finally excludes the structure (III)



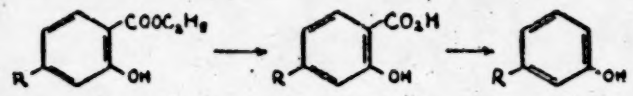
Hence, the cyclization of the ketovinylation product (I) proceeds in such a way that the carbonyl group of the ketovinyl residue reacts with the methyl of the acetyl group. Attempts were made to detect the presence of the second possible cyclization product (III), but we did not succeed in isolating this substance; it is evidently not formed in any appreciable amount. The reaction that we have discovered is of interest as a preparative method, inasmuch as all of the accepted methods for the preparation of 4-alkylsalicylic acids are based on the carbonation of m-alkylphenols [4, 5] or on related reactions [6-9]. However, the source of the required m-alkylphenols is coal tar, and no satisfactory synthetic methods of obtaining these, particularly the higher homologs, are known. We therefore attempted to extend our reaction to the preparation of the higher homologs of the 4-alkylsalicylic acids, and we obtained modest, but positive results. The higher alkyl 2-chlorovinyl ketones, namely, the ethyl, propyl, and isobutyl ketones, were found to react with ethyl acetoacetate under the same conditions in accordance with the same scheme, the corresponding 4-alkylsalicylic esters being formed; the yields of the latter, however, were low (about 20%). The reaction is evidently more complex, but in this case also the substituted salicylic ester was isolated without great difficulty. Special attention was again paid to the question of the structure of the substance isolated, for there were two possibilities in the cyclization:



It was found that only one of the possible isomers was formed, and attempts to detect the second isomer were not successful. The structures of the products were proved by experiments on the product of the condensation of 2-chlorovinyl propyl ketone with ethyl acetoacetate, which was taken as typical. Hydrolysis and decarboxylation gave a

phenol having the properties of m-propylphenol, and methylation with dimethyl sulfate followed by oxidation gave methoxyterephthalic acid as sole product. This indicates that the course of the condensation reaction of higher alkyl 2-chlorovinyl ketones is the same as that of 2-chlorovinyl methyl ketone.

The 4-alkylsalicylic esters obtained are colorless oily liquids that can be preserved without change for a long time. The corresponding acids were prepared by hydrolysis with aqueous alkali; these are readily crystallizing solids (yields 60-90%). By decarboxylation of the acids, which proceeds smoothly by pyrolysis, high yields were obtained of the corresponding m-alkylphenols:



In view of the ready accessibility of the starting materials, the proposed method for the synthesis of inaccessible m-alkylphenols is undoubtedly of interest, in spite of the low yields obtained in the first stage of the synthesis.

EXPERIMENTAL

1. Ethyl 4-Methylsalicylate. A mixture of 260 g (2 moles) of ethyl acetoacetate, 30 g (0.22 mole) of finely ground potassium carbonate, and 100 ml of absolute toluene was prepared in a three-necked flask fitted with stirrer, dropping funnel, and reflux condenser and was boiled while being vigorously stirred. A solution of 21 g (0.2 mole) of 2-chlorovinyl methyl ketone in 100 ml of absolute toluene was added dropwise to the constantly heated mixture over a period of eight hours, and the mixture was then heated further for about one hour and left overnight. The precipitate was filtered off and washed carefully with benzene, and benzene and toluene were then distilled from the combined filtrates at 50-60 mm, and ethyl acetoacetate (about 100 g) was distilled off at 10 mm. The residue was vacuum-distilled, and a wide fraction boiling at 128-150° (10-30 mm) was collected; this was redistilled and yielded a fraction boiling at 128-132° (7 mm). Redistillation gave 14.2 g (39.2%) of ethyl 4-methylsalicylate, b.p. 129-132° (11 mm); d_4^{20} 1.0915; n_D^{25} 1.5174.

For ethyl 4-methylsalicylate the literature gives: b.p. 254° (760 mm)[10]; b.p. 133° (12 mm), d_4^{20} 1.0950 [11].

Found %: C 67.32; 67.26; H 7.04; 7.06

$C_{10}H_{12}O_3$. Calculated %: C 66.65; H 6.71

Ethyl 4-methylsalicylate is a colorless stable liquid. It gives a violet color with aqueous ferric chloride, and it forms a voluminous white precipitate of the phenoxide with aqueous caustic soda.

2. Ethyl 4-Ethylsalicylate. Reaction between 260 g (2 moles) of ethyl acetoacetate, 23.7 g (0.2 mole) of 2-chlorovinyl ethyl ketone, and 30 g of potassium carbonate in toluene was carried out as described above. When reaction was complete, 200 ml of water was added, and the toluene layer was separated and washed with two 100-ml portions of water. The aqueous extracts were extracted with three 100-ml portions of ether, and the ether extracts were combined with the toluene solution. The solution was dried over magnesium sulfate and distilled. The ether and toluene were distilled off at 30 mm, and the residue, distilled at 10 mm, yielded: Fraction I, b.p. up to 95°; Fraction II, b.p. 95-130°; and Fraction III, b.p. 130-152°. In a redistillation of Fraction II, distillate coming over below 112° (9 mm) was rejected, and the residue was combined with Fraction III. Two distillations of this combined fraction gave a substance of b.p. 129-133° (9 mm), which, when distilled once further, gave 5.8 g (18%) of ethyl 4-ethylsalicylate, b.p. 141-142° (15 mm); d_4^{20} 1.0784; n_D^{20} 1.5162. It is a stable colorless oily liquid, which gives a violet color with aqueous ferric chloride.

3. Ethyl 4-Propylsalicylate. Reaction between 286 g (2.2 moles) of ethyl acetoacetate, 29.5 g of 2-chlorovinyl propyl ketone, and 32 g (0.23 mole) of potassium carbonate in 250 ml of absolute xylene was carried out as described above. After treatment described for the preceding experiment, distillation yielded a fraction of b.p. 110-150° (6 mm). This was boiled with a sodium ethoxide solution (2 g of sodium in 50 ml of absolute alcohol) for two hours, and was then poured into 1500 ml of 2% sulfuric acid. The mixture was extracted with ether, and the extract was dried over sodium sulfate. The ether was distilled off, and the residue was distilled under reduced pressure, a fraction of b.p. 135-140° (6 mm) being collected. Redistillation yielded 7.7 g (17%) of ethyl 4-propylsalicylate, b.p. 138-140° (6 mm); d_4^{20} 1.0836 n_4^{20} 1.5165.

Found %: C 68.95; 69.14; H 7.70; 7.72

$C_{12}H_{16}O_3$. Calculated %: C 69.20; H 7.75

Ethyl 4-propylsalicylate is a colorless stable liquid. It gives a violet color with aqueous ferric chloride.

4. Ethyl 4-Isobutylsalicylate. Reaction between 164 g (1.26 moles) of ethyl acetoacetate, 18.5 g (0.12 mole) of 2-chlorovinyl isobutyl ketone, and 30 g (0.22 mole) of potassium carbonate in 150 ml of absolute xylene was carried out as described above. After the treatment described for the preparation of ethyl 4-ethylsalicylate, distillation gave a fraction of b.p. 145-152° (8 mm). Redistillation gave 4.9 g (18%) of ethyl 4-isobutylsalicylate, b.p. 148.5-150° (9 mm); d_4^{20} 1.0878; n_D^{20} 1.5118.

Ethyl 4-isobutylsalicylate is a colorless stable oil. It gives a violet color with alcoholic ferric chloride.

5. 4-Methylsalicylic Acid. A mixture of 13.2 g (0.075 mole) of ethyl 4-methylsalicylate with a solution of 8.4 g (0.15 mole) of caustic potash in 200 ml of water was boiled until all traces of oil disappeared (about two hours). The solution was cooled and extracted with ether, and air was passed through the aqueous layer to remove traces of ether. The aqueous layer was carefully acidified with 5% hydrochloric acid. The precipitate was filtered off, washed with cold water, and dried in a vacuum. Recrystallization from water gave 10 g (90%) of colorless needles, m.p. 175°. For 4-methylsalicylic acid the literature [12] gives m.p. 175°.

Found %: C 63.33; 63.31; H 5.49; 5.31

$C_8H_8O_3$. Calculated %: C 63.15; H 5.30

4-Methylsalicylic acid is readily soluble in alcohol and in ether; it is moderately soluble in hot water, and only slightly soluble in cold water. It gives a violet color with an aqueous solution of ferric chloride.

6. 4-Ethylsalicylic Acid. This acid was prepared in a similar way by the hydrolysis of 1.94 g of ethyl 4-ethylsalicylate. Recrystallization from water gave 1.16 g (70%) of colorless needles, m.p. 124°. For 4-ethylsalicylic acid the literature [6] gives m.p. 124°.

4-Ethylsalicylic acid is readily soluble in alcohol and in ether; it is very difficultly soluble in cold water, more readily in hot water. It gives a violet color with an aqueous solution of ferric chloride.

7. 4-Propylsalicylic Acid. This acid was prepared in a similar way by the hydrolysis of 2.0 g of ethyl 4-propylsalicylate. Recrystallization from water gave 5.8 g (90%) of colorless needles, m.p. 113°.

Found %: C 66.76; 66.67; H 6.94; 7.02

$C_{10}H_{12}O_3$. Calculated %: C 66.65; H 6.71

4-Propylsalicylic acid is readily soluble in alcohol and in ether, and is sparingly soluble in hot water. It gives a violet color with an aqueous solution of ferric chloride.

8. 4-Isobutylsalicylic Acid. This acid was prepared in a similar way by the hydrolysis of 2.8 g of ethyl 4-isobutylsalicylate. Recrystallization from a large volume of water yielded 1.5 g (62%) of colorless crystals, m.p. 87°.

Found %: C 68.12; H 7.47

$C_{11}H_{14}O_3$. Calculated %: C 68.02; H 7.27

4-Isobutylsalicylic acid is readily soluble in alcohol and in ether; it is insoluble in cold water, and is sparingly soluble in hot water. It gives a violet color with aqueous ferric chloride.

9. m-Cresol. A small distillation flask containing 3.8 g (0.025 mole) of 4-methylsalicylic acid was heated in a metal bath. At 275° the molten substance began to froth, and as decarboxylation occurred, so m-cresol distilled over. Redistillation gave 1.7 g (63%) of m-cresol, b.p. 201-202°; d_4^{20} 1.0253; n_D^{20} 1.5317; found MR 32.66; calculated for C_7H_8O: MR 32.42. The literature [13, 14] gives for m-cresol: b.p. 201°, d_4^{20} 1.034; d_4^{18} 1.0363; n_D^{18} 1.5424.

Its benzoic ester was prepared in the usual way: glistening scales, m.p. 54° (from aqueous alcohol). The literature [15] give 54°.

10. m-Ethylphenol. This was prepared similarly from 2.6 g of 4-ethylsalicylic acid. Redistillation gave 1.4 g (70%) of m-ethylphenol, b.p. 217-218°; d_4^{20} 1.0218; n_D^{20} 1.5296; found MR 36.91; calculated for $C_8H_{10}O$: MR 37.07. The literature [16, 17] gives for m-ethylphenol: b. p. 217°; d_4^{15} 1.0230; n_D^{18} 1.5340.

Its 3,5-dinitrobenzoic ester was prepared in the usual way by heating the substance with 3,5-dinitrobenzoyl chloride in pyridine. Recrystallization from alcohol gave light-yellow plates, m. p. 107°.

Found %: N 9.00; 9.08

Calculated %: N 8.86

11. m-Propylphenol. This was prepared similarly from 5.8 g of 4-propylsalicylic acid. Redistillation gave 3.6 g (85%) of m-propylphenol, b.p. 229-231°; d_4^{20} 0.9877; n_D^{20} 1.5223; found MR 42.07; calculated for $C_9H_{12}O$ a MR 41.69. The literature [18] gives for m-propylphenol: b.p. 117-118° (12 mm).

Found %: C 79.15; 79.20; H 8.82; 8.95

Calculated %: C 79.36; H 8.88

Its 3,5-dinitrobenzoic ester was prepared in the usual way. Recrystallization from aqueous alcohol gave light-yellow plates, m.p. 75°. For m-propylphenyl 3,5-dinitrobenzoate the literature [19] gives m.p. 77°.

12. Methylation and Oxidation of 4-Methylsalicylic Acid. A mixture of 7.6 g (0.05 mole) of 4-methylsalicylic acid and 12 ml (0.13 mole) of dimethyl sulfate was shaken for 30 minutes with a solution of 2.5 g of caustic soda in 30 ml of water. The mixture was heated to the boil, a further 4 g of caustic soda was added, and boiling was continued for four hours. The cooled mixture was acidified, and the precipitate was filtered off, washed with water, dissolved in a small amount of 3% potassium carbonate solution, and, in order to remove any original 4-methylsalicylic acid, treated with small amounts of potassium permanganate until there was a permanent coloration. The filtered solution was acidified, and the crystals of 4-methyl-o-anisic acid that separated were filtered off and subjected to oxidation without further purification. The oxidation was carried out by heating 0.08 g of the substance with excess of potassium permanganate in 30 ml of water at the boil for eight hours. The excess of permanganate was destroyed by the addition of alcohol, and the mixture was filtered. The filtrate was acidified and extracted with ether. The ether extract was extracted with 25 ml of 3% caustic soda. Air was blown through the alkaline solution to remove ether. The solution was then acidified, and the crystals of methoxyterephthalic acid that separated were filtered off. Recrystallization from water yielded colorless crystals, m.p. 280°. For methoxyterephthalic acid the literature [20] gives m.p. 281°.

13. 4-Propyl-o-anisic Acid. A mixture of 1.04 g (0.006 mole) of 4-propylsalicylic acid and 4 ml (0.006 mole) of dimethyl sulfate was shaken for 45 minutes with a solution of 0.5 g of caustic soda in 20 ml of water. The mixture was heated to the boil, 30 ml of 10% caustic soda was added, and boiling was continued for six hours. After the treatment described for the preceding experiment a crystalline precipitate was obtained. Recrystallization from aqueous alcohol gave colorless crystals, m.p. 80.5°.

Found %: C 67.89; 67.73; H 7.16; 7.13

$C_{11}H_{14}O_3$. Calculated %: C 68.02 H 7.27

4-Propyl-o-anisic acid is readily soluble in alcohol and in ether, but is almost insoluble in water. It does not give a color with ferric chloride solution.

14. Oxidation of 4-Propyl-o-anisic Acid. The oxidation of the acid (0.64 g) was carried out as described for Experiment 12. Recrystallization from water gave methoxyterephthalic acid, m.p. 291°. In admixture with the substance obtained in Experiment 12 there was no depression in melting point.

SUMMARY

1. By the condensation of alkyl 2-chlorovinyl ketones with ethyl acetoacetate in presence of potassium carbonate in an inert solvent, the corresponding 4-alkylsalicylic esters were obtained. The possible mechanism of the reaction is examined.

2. The structure of the resulting compounds was proved by methylating the methyl and propyl homologs and then oxidizing the products to methoxyterephthalic acid.

3. The 4-alkylsalicylic esters were hydrolyzed with aqueous alkali to the corresponding acids, and these were then decarboxylated with formation of the corresponding m-alkylphenols in good yield.

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REACTION OF 2-CHLOROVINYL KETONES WITH ANTHRACENE

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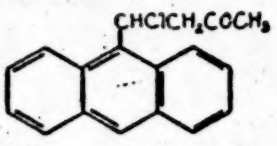
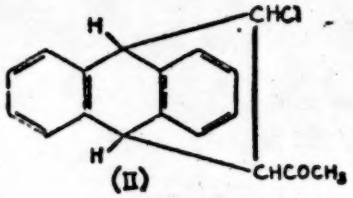
Investigation of the ketovinylation reaction has shown that, like acid anhydrides, 2-chlorovinyl ketones condense with aromatic compounds in presence of Friedel-Crafts catalysts; in this way substituted styryl ketones may be prepared [1]. On the other hand, 2-chlorovinyl keytones readily undergo the diene-synthesis reaction with hydrocarbon dienes (cyclopentadiene, aliphatic dienes; [2, 3]. It was of interest, therefore, to determine which of these two processes would occur in the reaction between a 2-chlorovinyl ketone and anthracene since it is well known that the anthracene molecule combines within itself the properties of an aromatic compound and a diene system. It was found that, in benzene solution at room temperature, 2-chlorovinyl methyl ketone does not react with anthracene: even after a long treatment, only the original substances could be isolated from the reaction mixture. A five-hour treatment in toluene also did not give positive results.

Very different behavior was found when the reaction was carried out in presence of an equimolecular amount of stannic chloride as catalyst. A new substance was then isolated from the reaction mixture, and analysis showed that this was formed by the addition of one molecule of 2-chlorovinyl methyl ketone to one molecule of anthracene. The resulting compound contained a carbonyl group, the presence of which was confirmed by the formation of the 2,4-dinitrophenylhydrazone and the azine. Oxidation of the adduct in acetone with potassium permanganate gave anthraquinone: this indicates that it is the meso carbon atoms of anthracene that are concerned in the condensation with 2-chlorovinyl methyl ketone, for it is known that oxidation of meso-substituted anthracenes always gives anthraquinone [4, 5], whereas anthracenes substituted in the side nuclei are oxidized to the corresponding anthraquinonecarboxylic acids [6].



(I)



(II)

Hence, there was a choice of two formulas (I) and (II) for structure of the adduct, i.e. either anthracene adds, by virtue of its mobile meso hydrogen atom, to the double bond of 2-chlorovinyl methyl ketone, or diene synthesis occurs with formation of 11-acetyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. It might be thought that formula (I) should be preferred, since numerous examples are known of the addition of aromatic hydrocarbons to α,β-unsaturated ketones in presence of Friedel-Crafts catalysts [7]. However, in the course of our investigation of the adduct, we found it necessary to reject this formula and to accept formula (II). It was found, in fact, that the ultraviolet absorption spectrum of our substance (Fig. 1) is close in form to that of the adduct formed by anthracene with maleic anhydride (Fig. 2), the values of λ_{max} being almost identical (λ_{max} = 265 and 273 mμ). These absorption curves are close in form to that of 9,10-dihydroanthracene, and are quite different from those of anthracene and its meso substitution products • [9].

We can, however, advance also purely chemical arguments in favor of formula (II). Thus, under the action of caustic alkali the adduct formed by anthracene with 2-chlorovinyl methyl ketone eliminates hydrogen chloride and gives an unsaturated ketone, differing in properties from the known 4-(9-anthryl)-3-buten-2-one [10], the formation of which would be expected if the formula of the adduct is (I).

• The absorption curves were determined with a Dianov-Klokov spectrophotometer [8] in the Laboratory for Physico-chemical Investigation of Organic Compounds of the Organic Chemistry Department of the Moscow State University.

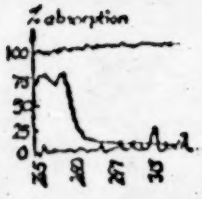


Fig. 1

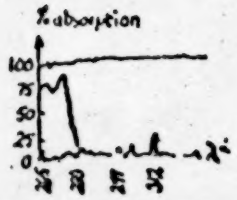
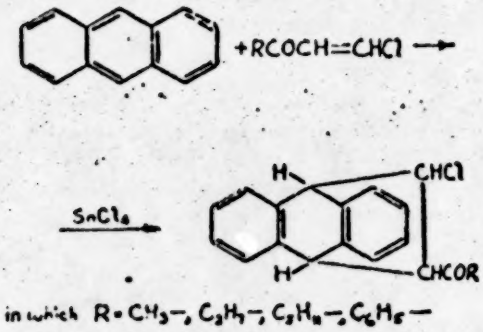


Fig. 2

Fig. 1. Ultraviolet absorption spectrum of the adduct formed by 2-chlorovinyl methyl ketone with anthracene (in dichloroethane solution).

Fig. 2. Ultraviolet absorption spectrum of the adduct formed by maleic anhydride with anthracene (in dichloroethane solution).

The condensation of 2-chlorovinyl ketones with anthracene was found to be fairly general. The reaction was carried out also on propyl, pentyl, and phenyl 2-chlorovinyl ketones. Reaction of these with anthracene in presence of stannic chloride in a medium of absolute benzene gave the corresponding adducts in yields of 70-84%.



in which R = CH_3–, C_3H_7–, C_5H_{11}–, C_6H_5–

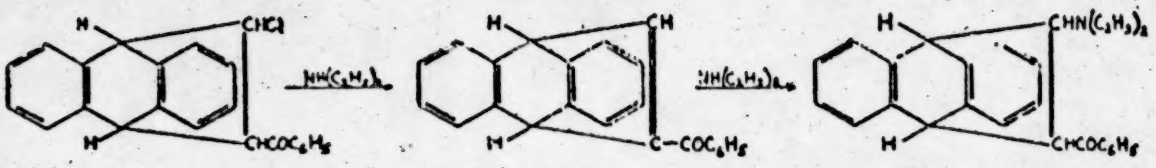
The 11-acyl-12-chloro-9,10-dihydro-9,10-ethanoanthracenes obtained in this way were found to be colorless crystalline substances which decompose with separation of anthracene when heated to 200°.

It must be emphasized that the diene condensation of 2-chlorovinyl ketones with anthracene will occur – and then, very readily – only in the presence of stannic chloride, although it is probable that other Friedel-Crafts catalysts could be used in our reaction. It is interesting that, when 2-chlorovinyl phenyl ketone was treated with anthracene in boiling xylene with passage of hydrogen chloride (as recommended by Barnett for the preparation of adducts of α,β-unsaturated ketones with anthracene [11]), 11-benzoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene was obtained in only 17% yield.

Like the methyl homolog, the other adducts of alkyl 2-chlorovinyl ketones with anthracene smoothly eliminated hydrogen chloride in presence of solid caustic soda in a medium of absolute ether, and good yields of 11-acyl-9,10-dihydro-9,10-ethenoanthracenes were obtained. These were found to be colorless crystalline substances, with the exception of 11-hexanoyl-9,10-dihydro-9,10-ethenoanthracene, which was obtained as a viscous noncrystallizing oil.

in which R = CH_3–, C_3H_7–, C_5H_{11}–

It is interesting that, under these conditions, the adduct formed by 2-chlorovinyl phenyl ketone with anthracene eliminates hydrogen chloride very slowly, the result of the reaction being a mixture of the original substance and unsaturated ketone, which is difficult to separate. With the object of isolating the pure unsaturated ketone, 11-benzoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene was boiled for two hours in diethylamine solution. The homogeneity of the medium then ensured the smooth elimination of hydrogen chloride, but it was found that the diethylamine itself reacted with some of the product by addition at the double bond, and the final product was a mixture of 11-benzoyl-9,10-dihydro-9,10-ethenoanthracene (26.7% yield) and 11-benzoyl-12-diethylamino-9,10-dihydro-9,10-ethanoanthracene (64.3% yield):



Treatment of the adduct formed by 2-chlorovinyl methyl ketone with alcoholic alkali yielded 11-acetyl-12-ethoxy-9,10-dihydro-9,10-ethanoanthracene. It is probable that here again the unsaturated ketone is formed in the first stage, and this then readily combines with an alcohol molecule at the double bond.

EXPERIMENTAL

1. 11-Acetyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. Stannic chloride (19 g) was added dropwise over a period of one hour to a vigorously-stirred mixture of 12.8 g of anthracene, 7.5 g of 2-chlorovinyl methyl ketone, and 200 ml of absolute benzene. The addition of the first few drops of stannic chloride caused the reaction mixture to turn brown. The whole of the anthracene gradually dissolved, and a fine precipitate of the complex formed. When the whole of the stannic chloride had been added, the mixture was stirred for a further five hours and then decomposed by adding dilute hydrochloric acid while cooling the reaction flask with ice water. The benzene layer was separated, washed several times with water, then washed with sodium carbonate solution, and then again with water. The solution was dried over calcium chloride, benzene was distilled off under reduced pressure, and the solid residue was recrystallized from acetic acid. Yield 17.8 g (87.6%); m.p. 145°.

Found %: C 76.11; 76.04; H 5.44; 5.35; Cl 12.40; 12.48

$C_{18}H_{15}OCl$ Calculated %: C 76.48; H 5.31; Cl 12.46

The substance forms colorless plates, readily soluble in hot acetic acid, in benzene, and in acetone. When heated to 200° it decomposes with separation of anthracene.

The azine was prepared by reaction with an alcoholic solution of hydrazine. It is a colorless powder, insoluble in most organic solvents; m.p. 162-164° (decomp.).

Found %: N 5.29; 5.19

$C_{36}H_{30}N_2Cl_2$. Calculated %: N 5.00

The 2,4-dinitrophenylhydrazone was prepared in a medium of glacial acetic acid and was recrystallized from the same solvent. It forms orange crystals, m.p. 278°.

Found %: N 12.22; 12.29

$C_{24}H_{19}O_6N_6Cl$ Calculated %: N 12.11

2. 11-Butyryl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. This substance was prepared similarly from 17 g of anthracene, 15.5 g of 2-chlorovinyl propyl ketone, and 25 g of stannic chloride in a medium of 250 ml of absolute benzene. The yield was 25 g (84.4%). After recrystallization, first from acetic acid, and then from absolute acetone, it melted at 93-94°.

Found %: C 77.64; H 6.13; Cl 11.57

$C_{20}H_{19}OCl$ Calculated %: C 77.28; H 6.16; Cl 11.40

It forms colorless crystals, readily soluble in hot acetic acid, in benzene, in acetone, and in ether. When heated to about 200°, it decomposes with separation of anthracene.

3. 11-Hexanoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. This substance was prepared similarly from 15 g of anthracene, 15 g of 2-chlorovinyl pentyl ketone, and 25 g of stannic chloride in 250 ml of absolute benzene. The solid residue remaining after removal of benzene was pressed out on a porous plate. The yield was 20 g (70.1%). After

recrystallization, first from glacial acetic acid, and then from acetone, it melted at 82°.

Found %: C 77.91; 78.11; H 6.85; 6.96; Cl 10.37; 10.68
$C_{12}H_{11}OCl$. Calculated %: C 77.97; H 6.84; Cl 10.41

It forms colorless crystals, soluble in acetic acid, benzene, acetone, and ether. When heated to about 200°, it decomposes with separation of anthracene.

4. 11-Benzoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. This substance was prepared similarly from 12.8 g of anthracene, 12 g of 2-chlorovinyl phenyl ketone, and 19 g of stannic chloride in a medium of 200 ml of absolute benzene. The yield was 20 g (80.6%). After recrystallization from glacial acetic acid and from acetone it melted at 184-186°.

Found %: C 80.08; 80.11; H 5.18; 5.03
$C_{21}H_{17}OCl$. Calculated %: C 80.10; H 4.96

It forms colorless crystals, soluble in acetic acid, toluene, and acetone.

5. Reaction of 2-Chlorovinyl Phenyl Ketone with Anthracene in Presence of Hydrogen Chloride. 2-Chlorovinyl phenyl ketone (6 g) was added to a suspension of 3 g of anthracene in 50 ml of absolute o-xylene. The mixture was boiled, and a stream of dry hydrogen chloride was passed through for ten hours. The undissolved anthracene was filtered off, and the filtrate was evaporated by heating it under reduced pressure (5 mm). Recrystallization of the residue from acetic acid yielded 1 g (16.8%) of adduct, m.p. 183-185°. In a mixture melting point test with 11-benzoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene there was no depression.

6. 11-Acetyl-9,10-dihydro-10-ethenoanthracene. Finely ground caustic soda (6 g) was added to a solution of 3 g of 11-acetyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene in 100 ml of absolute ether, and the mixture was shaken vigorously for ten hours. The solution was then filtered and evaporated under reduced pressure. The solid residue was recrystallized from absolute acetone; yield 2 g (76.9%); m.p. 174-175°.

Found %: C 87.77; 87.57; H 5.78; 5.88
$C_{16}H_{14}O$. Calculated %: C 87.80; H 5.73

The substance forms colorless crystals, soluble in ether, acetone, and benzene.

7. 11-Butyryl-9,10-dihydro-9,10-ethenoanthracene. This was prepared similarly by treatment of 2 g of 11-butyryl-12-chloro-9,10-dihydro-9,10-ethanoanthracene with 6 g of finely ground caustic soda in 100 ml of absolute ether. The yield was 1.4 g (79.5%). After recrystallization from dry acetone it melted at 151-153°.

Found %: C 87.78; 87.57; H 6.50; 6.55
$C_{18}H_{18}O$. Calculated %: C 87.55; H 6.61

The substance forms colorless crystals, soluble in ether, benzene, and acetone.

8. 11-Hexanoyl-9,10-dihydro-9,10-ethenoanthracene. This was prepared similarly by treatment of 3 g of 11-hexanoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene with 10 g of finely ground caustic soda in 50 ml of absolute ether. The residue after removal of ether was a noncrystallizing viscous oil, which was dried under reduced pressure (7 mm) at 80° in presence of phosphoric oxide. Yield 2.5 g (96%); n_D^{25} 1.5900.

Found %: C 87.11; H 7.30
$C_{22}H_{24}O$. Calculated %: C 87.37; H 7.25

9. Reaction of 11-Benzoyl-12-chloro-9,10-dihyrdo-9,10-ethanoanthracene with Diethylamine. 11-Benzoyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene (3.3 g) was added to 50 ml of diethylamine, and the mixture was refluxed for two hours and then set aside for one day at room temperature. The excess of diethylamine was then distilled off, 100-150 ml of 5% hydrochloric acid was added to the residue, and the resulting mixture was extracted with ether (the aqueous layer was kept). The ether extract was washed several times with 5% hydrochloric acid and then with water (the washings were added to the hydrochloric acid solution). After being dried over sodium sulfate, the ether layer was distilled, and yielded 0.77 g (26.3%) of 11-benzoyl-9,10-dihydro-9,10-ethenoanthracene, m.p. 162-163° after recrystallization from dry acetone.

Found %: C 89.62; 89.59; H 5.36; 5.27
$C_{23}H_{18}O$. Calculated %: C 89.59; H 5.23

The hydrochloric acid solution was extracted several times with ether, and then 10% caustic soda was added until a white precipitate separated. The precipitate was rapidly filtered off, washed with water, and twice reprecipitated with alkali from solution in 5% hydrochloric acid. The yield of 11-benzoyl-12-diethylamino-9,10-dihydro-9,10-ethanoanthracene was 2.35 g (64.3%). After recrystallization from aqueous methanol it melted at 52-54°.

The substance forms a difficultly crystallizable yellowish powder, readily soluble in alcohol, ether, acetone, and petroleum ether.

Its picrate was prepared in methanol and recrystallized from the same solvent: lemon-yellow needles, m.p. 187-188°.

Found %: N 9.39; 9.54

$C_{32}H_{30}O_8N_4$. Calculated %: N 9.18

10. 11-Acetyl-12-ethoxy-9,10-dihydro-9,10-ethanoanthracene. A mixture of 0.88 g of 11-acetyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene, 0.6 g of caustic soda, and 15 ml of ethanol was shaken at room temperature for three hours. A precipitate of sodium chloride formed. The reaction mixture was poured into 70 ml of water. The white precipitate that separated was filtered off and washed on the filter with several successive portions of water. The yield was 0.8 g (87.8%). After recrystallization from acetone it melted at 162-164°.

Found %: C 82.36; H 6.90

$C_{20}H_{20}O_2$. Calculated %: C 82.19; H 6.90

SUMMARY

1. 2-Chlorovinyl ketones react with anthracene in accordance with the scheme of the diene synthesis.

2. It is shown for the first time that stannic chloride is a catalyst for the diene-synthesis reaction.

3. The 11-acyl-12-chloro-9,10-dihydro-9,10-ethanoanthracenes formed in this reaction are reactive substances and can be used as starting materials for the synthesis of various 9,10-ethanoanthracene derivatives.

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 10. DIESTERS OF 2-ALKOXY- AND 2-PHENOXY-VINYLPHOSPHONODITHIOLIC AND OF 2-ALKOXY- AND 2-PHENOXY-VINYL PHOSPHONOTRITHIOIC ACIDS

K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

Possible methods for the synthesis of diesters of 2-alkoxy- and 2-phenoxy-vinylphosphonodithiolic acids are 1) the action of 2-alkoxy- and 2-phenoxy-vinylphosphonic dichlorides on thiols in the presence of pyridine, and 2) the action of 2-alkoxy- and 2-phenoxy-vinylphosphonic dichlorides on sodium mercaptides.

The first reaction proved to be satisfactory only in the preparation of S,S-diphenyl 2-isobutoxyvinylphosphonodithioate; in all other cases we were unable to isolate the substance in the pure state, since it decomposed during vacuum distillation. By the second method, which has been extensively used by A. E. Arbuzov [1], we were able to prepare the diethyl esters of 2-ethoxy-, 2-butoxy-, 2-isobutoxy, and 2-phenoxy-vinylphosphonodithiolic acids. These compounds are slightly yellow liquids which can be readily distilled under reduced pressure. They are soluble in the usual organic solvents, but insoluble in water. Table 1 gives the constants of the esters obtained.

We prepared diesters of 2-alkoxy- and 2-phenoxy-vinylphosphonotrithioic acids by a method analogous to the second method. These esters are thick yellowish liquids. They are readily soluble in organic solvents, but are insoluble in water. Properties of these esters are given in Table 2.

TABLE 1

Formula of substance	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_2H_5-O-CH=CHPO(S-C_2H_5)_2$	135 (2)	1.5475	1.1366
$n-C_4H_9-O-CH=CHPO(S-C_2H_5)_2$	154 (2)	1.5544	1.1410
$i-C_4H_9-O-CH=CHPO(S-C_2H_5)_2$	145 (2)	1.5370	1.0961
$i-C_4H_9-O-CH=CHPO(S-C_6H_5)_2$	m.p. 72–73		
$C_6H_5-O-CH=CHPO(S-C_2H_5)_2$	162 (1)	1.5800	1.1535

TABLE 2

Formula of substance	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_2H_5-O-CH=CHPS(S-C_2H_5)_2$	134 (1)	1.5858	1.1734
$i-C_3H_7-O-CH=CHPS(S-C_2H_5)_2$	136 (2)	1.5672	1.1198
$i-C_4H_9-O-CH=CHPS(S-C_2H_5)_2$	145 (1)	1.5662	1.1060
$C_6H_5-O-CH=CHPS(S-C_2H_5)_2$	155 (1)	1.6336	1.3142

EXPERIMENTAL

S,S-Diethyl 2-Ethoxyvinylphosphonodithioate $C_2H_5-O-CH=CHPO(SC_2H_5)_2$. Sodium (2.3 g) was prepared for reaction by Bruhl's method and added to 150 ml of absolute ether; the mixture was cooled while 9 g of ethanethiol was added. On the next day a solution of 9.45 g of 2-ethoxyvinylphosphonic dichloride in an equal volume of ether was added with stirring. When reaction was complete, the ether layer was poured off and dried over calcined sodium sulfate. The ether was distilled off, and vacuum fractionation of the residue gave 6.7 g (55.8%) of product. After the third fractionation it had b.p. 135° (2 mm); n_D^{20} 1.5475; d_4^{20} 1.1366.

Found %: P 12.75; 12.77

$C_8H_{17}O_3S_2P$. Calculated %: P 12.91

S,S-Diethyl 2-Butoxyvinylphosphonodithioate n-$C_4H_9-O-CH=CHPO(SC_2H_5)_2$. Sodium wire (2 g) was added to 150 ml of absolute ether contained in a three-necked flask fitted with stirrer. The flask was cooled, and a solution of 9 g of ethanethiol in an equal volume of ether was added slowly from a dropping funnel. When the whole of the thiol had been added, a few pieces of sodium were introduced into the flask and the reaction mixture was set aside overnight. On the next day the mixture was heated for two hours at 30° in a water bath and the pieces of sodium were removed. The mixture was cooled, and a solution of 11.85 g of 2-butoxyvinylphosphonic dichloride in 15 ml of ether was added. When reaction was complete, the ether layer was poured off, the precipitate was washed twice with ether, and the filtrate was dried over sodium sulfate and vacuum-fractionated: b.p. 154° (2 mm); d_4^{20} 1.1410; n_4^{20} 1.5544; yield 7.6 g (52%).

Found %: P 11.37; 11.38

$C_{10}H_{21}O_3S_2P$. Calculated %: P 11.36

S,S-Diethyl 2-Isobutoxyvinylphosphonodithioate i-$C_4H_9-O-CH=CHPO(SC_2H_5)_2$. 2-Isobutoxyvinylphosphonic dichloride (11.85 g) was added with stirring and cooling to sodium mercaptide prepared in absolute ether from 2.3 g of Brühl sodium and 9 g of ethanethiol. The product isolated amounted to 9 g (63%) and had b.p. 145° (2 mm); n_D^{20} 1.5370; d_4^{20} 1.0961.

Found %: P 11.34; 11.41

$C_{10}H_{21}O_3S_2P$. Calculated %: P 11.56

S,S-Diphenyl 2-Isobutoxyvinylphosphonodithioate i-$C_4H_9-O-CH=CHPO(SC_6H_5)_2$. Pyridine (7.2 g) and benzenethiol (10 g) were added to 150 ml of dry benzene, and the resulting mixture was stirred and cooled slightly while a solution of 10 g of 2-isobutoxyvinylphosphonic dichloride in 10 ml of benzene was added from a dropping funnel over a period of one hour. When the whole of the acid chloride had been added the mixture was set aside overnight. On the next day the precipitate of pyridine hydrochloride was filtered off. The filtrate was treated with 3% sodium carbonate solution and dried with sodium sulfate. Benzene was distilled off, and 12 g of crude crystalline product was isolated. Recrystallization from petroleum ether gave 10 g (60%) of pure product, m.p. 72-73°.

Found %: C 59.43; 59.49; H 5.93; 6.09

$C_{18}H_{21}O_3PS_2$. Calculated %: C 59.34 H 5.77

S,S-Diethyl 2-Phenoxyvinylphosphonodithioate $C_6H_5-O-CH=CHPO(SC_2H_5)_2$. A solution of 9.5 g of ethanethiol in 20 ml of ether was added gradually to a cooled slowly stirred mixture of 2.3 g of Brühl sodium and 200 ml of absolute ether contained in a three-necked flask. The resulting mercaptide was left overnight. On the next day 11.85 g of 2-phenoxyvinylphosphonic dichloride was added with stirring. When reaction was complete the ether layer was poured off. The filtrate was dried over calcined sodium sulfate and fractionated. The product, amounting to 9 g, had b.p. 162° (1 mm); n_D^{20} 1.5860; d_D^{20} 1.1535.

Found %: P 10.55; 10.74

$C_{12}H_{17}O_3S_2P$. Calculated %: P 10.76

Diethyl 2-Ethoxyvinylphosphonothiolthioate $C_2H_5-O-CH=CH-PS(SC_2H_5)_2$. Brühl sodium (2.3 g) was added to absolute ether contained in a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. With cooling and slow stirring, a solution of 9.5 g of ethanethiol in an equal volume of ether was added. On the next day the mixture was heated for one hour at 30-35° in a water bath, and to the sodium ethylmercaptide so formed 10.2 g of 2-ethoxyvinylphosphonothioic dichloride was added from a dropping funnel. When addition of the acid chloride was complete, the mixture was set aside overnight and then heated at 30-35° for two hours. The precipitate was filtered off, and the filtrate was dried over calcined sodium sulfate. After removal of ether the residue was vacuum-fractionated and yielded 8.4 g (65.9%) of substance of b.p. 134° (1 mm); n_D^{20} 1.5858, d_4^{20} 1.1734.

Found %: C 37.46; 37.21; H 6.41; 6.29

$C_8H_{17}OPS_2$ Calculated %: C 37.50; H 6.30

Diethyl 2-Isopropoxyvinylphosphonotrithioate i-C_3H_7-O-CH = CH-PS(SC_2H_5)$_2$. A solution of 10.95 g of 2-isopropoxyvinylphosphonothioic dichloride in 15 ml of ether was added to sodium ethylmercaptide, prepared from 2.3 g of sodium and 9 g of ethanethiol in 300 ml of absolute ether. When the whole of the acid chloride had been added, the reaction mixture was set aside overnight. On the next day the mixture was heated in a water bath at 30° and the ether layer was poured off. The filtrate was dried over sodium sulfate. The product, amounting to 8 g (59.2%), had b.p. 136° (2 mm): n_D^{18} 1.5672; d_4^{19} 1.1198.

Found %: C 40.09; 40.34 H 6.13; 6.73
$C_9H_{19}OPS_3$. Calculated %: C 40.00; H 7.03

Diethyl 2-Isobutoxyvinylphosphonotrithioate i-C_4H_9-O-CH = CHPS(SC_2H_5)$_2$. Sodium ethylmercaptide, prepared from 9 g of ethanethiol and 2.3 g of Brühl sodium, was placed in a flask, and 11.65 g of 2-butoxyvinylphosphonothioic dichloride was added gradually over a period of two hours. The reaction mixture was then set aside overnight. On the next day the mixture was warmed, and the ether layer was poured off and vacuum-fractionated. The yield of pure product was 8.6 g (60%), and it had b. p. 145° (1 mm); n_D^{19} 1.5662; d_4^{19} 1.1060.

Found %: C 42.63; 42.76; H 7.27; 7.36
$C_{10}H_{21}OPS_3$. Calculated %: C 42.25; H 7.39

Diethyl 2-Phenoxyvinylphosphonotrithioate C_6H_5-O-CH = CHPS(SC_2H_5)$_2$. A solution of 12.65 g of 2-phenoxyvinylphosphonothioic dichloride in 15 ml of absolute ether was added with stirring and cooling to sodium ethylmercaptide, prepared from 2.3 g of sodium and 9.5 g of ethanethiol in 250 ml of absolute ether. When the whole of the acid chloride had been added, the reaction mixture was set aside overnight. On the next day the mixture was warmed at 20° for two hours, and the ether layer was poured off and vacuum-fractionated. The product, amounting to 7.2 g (47%), had b.p. 155° (1 mm); n_D^{19} 1.5336; d_4^{19} 1.3142.

Found %: P 10.42; 10.27
$C_{12}H_{17}OPS_3$. Calculated %: P 10.19

SUMMARY

1. By the action of 2-ethoxy-, 2-butoxy-, 2-isobutoxy-, and 2-phenoxy-vinylphosphonic dichlorides on sodium ethylmercaptide, the diethyl esters of the corresponding 2-alkoxy-and 2-phenoxy-vinylphosphonodithiolic acids were prepared.

2. The diethyl esters of 2-ethoxy-, 2-isopropoxy-, 2-isobutoxy-, and 2-phenoxy-vinylphosphonotrithioic acids were synthesized by the reaction of sodium ethylmercaptide with the corresponding phosphonothioic dichlorides.

3. S,S-Diphenyl 2-isobutoxyvinylphosphonodithioate was prepared by the action of 2-isobutoxyvinylphosphonic dichloride on benzenethiol in presence of pyridine.

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 11. DIESTERS OF 2-(2-ALKOXYETHOXY)VINYLPHOSPHONIC ACIDS

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We prepared diesters of 2-(2-alkoxyethoxyl)vinylphosphonic acids by reaction of acid chlorides with alcohols in presence of pyridine in a benzene medium, following the method of Milobendzsky and Sakhnovsky [1]:

$$ROCH_2-CH_2-O-CH=CHPOCl_2 + 2ROH + 2C_5H_5N =$$
$$= ROCH_2-CH_2-O-CH=CHPO(OR)_2 + 2C_5H_5\cdot N\cdot HCl.$$

By this method we prepared the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, diheptyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-(2-methoxyethoxy)-, 2-(2-ethoxyethoxy)-, and 2-(2-butoxyethoxy)-vinyl-phosphonic acids in yields of up to 88%. The diesters of 2-(2-alkoxyethoxy)vinylphosphonic acids are colorless liquids that can be readily distilled under reduced pressure. They are soluble in many organic solvents, and some are soluble in water. Tables 1-3 give the constants of the esters we have synthesized.

TABLE 1

Formula of substance	B.p., °C (p in mm)	n_D^{20}	d_4^{20}	Yield (%)
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$	124 (1)	1.4590	1.1747	77.9
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$	134 (1)	1.4525	1.1067	76
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$	143 (1)	1.4510	1.0585	88
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}i)_2$	134 (2)	1.4469	1.0529	77
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}n)_2$	153 (1)*	1.4518	1.0354	75
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}i)_2$	148 (1)	1.4500	1.0341	77
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_3H_5)_2$	160 (2)	1.4789	1.1082	80
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	180 (1)	1.4540	1.0004	80
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_7H_{15}\text{-}n)_2$	190 (1)	1.4562	0.9845	62
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2OCH_3)_2$	171 (1)	1.4620	1.1467	70
$CH_3-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	175 (1)	1.4570	1.1088	76

TABLE 2

Formula of substance	B.p., °C (p in mm)	n_D^{20}	d_4^{20}	Yield (%)
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$	126 (2)	1.4528	1.1429	76
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$	133.5 (2)	1.4512	1.0812	78
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$	140 (2)	1.4510	1.0470	80
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}i)_2$	125 (2)	1.4452	1.0341	72
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}i)_2$	143 (2)	1.4492	1.0159	82
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_5)_2$	138.5 (2)	1.4702	1.0854	77
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_7H_{15}\text{-}n)_2$	200 (1)	1.4546	0.9745	88
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	163 (1)	1.4602	1.1279	84
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	180 (1)	1.4546	1.0917	86

TABLE 3

Formula of substance	B.p., °C (p in mm)	n_D^{20}	d_4^{20}	Yield (%)
$n\text{-}C_4H_9\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OCH_3)_2$	132 (1)	1.4565	1.1100	77
$n\text{-}C_4H_9\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OC_2H_5)_2$	155 (2)	1.4519	1.0815	79
$n\text{-}C_4H_9\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OC_3H_7\text{-}n)_2$	163 (2)	1.4529	1.0199	83
$n\text{-}C_4H_9\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OC_4H_9\text{-}n)_2$	180 (2)	1.4532	1.0008	83
$n\text{-}C_4H_9\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(O\text{-}C_4H_9\text{-}i)_2$	172 (2)	1.4512	1.0002	83
$n\text{-}C_4H_9\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OC_5H_5)_2$	152 (1)	1.4860	1.0530	71
$n\text{-}C_4H_9\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OC_6H_{13}\text{-}n)_2$	202 (2)	1.4550	0.9794	85
$n\text{-}C_4H_9\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OC_7H_{15}\text{-}n)_2$	207 (1)	1.4553	0.9644	89
$n\text{-}C_4H_9\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OCH_2\text{-}\text{-}CH_2\text{-}O\text{-}C_2H_5)_2$	193 (2)	1.4561	1.0643	87

EXPERIMENTAL

2-(2-Methoxyethoxy)vinylphosphonic Esters

Dimethyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OCH_3)_2$. A mixture of 100 ml of dry benzene, 8.5 g of absolute methanol, and 8 g of pyridine was prepared in a flask fitted with stirrer, reflux condenser, and dropping funnel. With stirring and cooling, 10.85 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride was added gradually. On the next day pyridine hydrochloride was filtered off, and the filtrate was washed with 3% sodium carbonate solution and dried over sodium sulfate. Vacuum fractionation yielded 8.5 g of substance (79% yield) having b.p. 124° (1 mm); n_D^{20} 1.4590; d_4^{20} 1.1747.

Found %: P 14.56; 14.60

$C_7H_{15}O_5P$. Calculated %: P 14.76

The preparation of the other esters was similar to that of dimethyl 2-(2-methoxyethoxy)vinylphosphonate.

Diethyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OC_2H_5)_2$. To a stirred cooled mixture of 5 g of absolute ethanol, 8 g of pyridine, and 80 ml of dry benzene, 10.95 g of 2-(2-methoxyethoxy)-vinylphosphonic dichloride was added. The product, amounting to 9 g (76%), had b.p. 134° (1 mm); n_D^{20} 1.4525; d_4^{20} 1.1067.

Found %: P 12.97; 13.00

$C_9H_{19}O_5P$. Calculated %: P 13.02

Dipropyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OC_3H_7\text{-}n)_2$. 2-(2-Methoxy-ethoxy)vinylphosphonic dichloride (12 g) was added with stirring to a mixture of 100 ml of dry benzene, 8.6 g of pyridine, and 6.6 g of absolute propyl alcohol. The product amounting to 12.9 g (88%), had b.p. 143° (1 mm); n_D^{20} 1.4510; d_4^{20} 1.0585.

Found %: P 11.54; 11.34

$C_{11}H_{23}O_5P$. Calculated %: P 11.65

Diisopropyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OC_3H_7\text{-}i)_2$. A solution of 15 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride in 15 ml of benzene was added to a mixture of 8.5 g of absolute isopropyl alcohol and 11 g of pyridine. The product, amounting to 14.5 g (77%), had b.p. 134° (2 mm); n_D^{20} 1.4469; d_4^{20} 1.0529.

Found %: P. 11.39; 11.33

$C_{11}H_{23}O_5P$. Calculated %: P 11.65

Dibutyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH{=}CHPO(OC_4H_9\text{-}n)_2$. 2-(2-Methoxy-ethoxy)vinylphosphonic dichloride (10.95 g) was added to a mixture of 7.4 g of absolute butyl alcohol and 8 g of pyridine. Vacuum fractionation yielded 12 g (80%) of a substance having b.p. 153° (1 mm); n_D^{20} 1.4518; d_4^{20} 1.0354.

Found %: P 10.27; 10.54

$C_{13}H_{27}O_5$. Calculated %: P 10.54

Diisobutyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(O-C_4H_9\text{-}i)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (12 g) was added to a mixture of 8.5 g of absolute isobutyl alcohol, 8.6 g of dry pyridine, and 60 ml of benzene. The product, amounting to 12.5 g (77%), had b.p. 148° (1 mm); n_D^{20} 1.4500; d_4^{20} 1.0341.

Found %: P 10.52; 10.55

$C_{12}H_{27}O_5P$. Calculated %: P 10.54

Diallyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_3H_5)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (9 g) was added to a mixture of 4.8 g of absolute allyl alcohol and 7 g of pyridine. The product, amounting to 8 g, had b.p. 160° (2 mm); n_D^{20} 1.4789; d_4^{20} 1.1082.

Found %: P. 11.36; 11.41

$C_{11}H_{19}O_5P$. Calculated %: P 11.45

Dihexyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (10.95 g) was added to a mixture of 10.3 g of absolute hexyl alcohol, 8 g of pyridine, and 120 ml of dry benzene. The product, amounting to 14 g (80%), had b.p. 180° (1 mm); n_D^{20} 1.4540; d_4^{20} 1.0004.

Found %: P 8.71; 8.56

$C_{17}H_{35}O_5P$. Calculated %: P 8.85

Diheptyl 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OC_7H_{15}\text{-}n)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (7.5 g) was added to a mixture of 8.5 g of absolute heptyl alcohol, 5.5 g of pyridine, and 100 ml of benzene. Vacuum fractionation yielded 9.3 g (79%) of product, b.p. 190° (1 mm); n_D^{20} 1.4562; d_4^{20} 0.9845.

Found %: C 59.93; 59.86; H 10.36; 10.52

$C_{19}H_{39}O_5P$. Calculated %: C 60.31; H 10.31

Bis(2-ethoxyethyl) 2-(2-Methoxyethoxy)vinylphosphonate $CH_3-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (15 g) was added to a mixture of 12.5 g of 2-ethoxyethanol, 11 g of pyridine, and 120 ml of dry benzene. Vacuum fractionation yielded 17 g (76%) of product, b.p. 175° (1 mm); n_D^{20} 1.4570; d_4^{20} 1.1088.

Found %: P 9.48; 9.32

$C_{13}H_{27}O_7P$. Calculated %: P 9.50

2-(2-Ethoxyethoxy)vinylphosphonic Esters

Dimethyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (9 g) was added to a mixture of 2.5 g of absolute methanol, 6.2 g of pyridine, and 60 ml of dry benzene. The product, amounting to 6.6 g (76%), had b.p. 126° (2 mm); n_D^{20} 1.4528; d_4^{20} 1.1429.

Found %: C 42.47; 42.60; H 7.69; 7.64

$C_8H_{17}O_5P$. Calculated %: C 42.85 H 7.58

Diethyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$. Reaction between 11.65 g of 2-(2-ethoxyethoxy)vinylphosphonic dichloride, 8 g of pyridine, and 5 g of absolute ethanol yielded 9.8 g (78%) of product, b.p. 133.5°, (2 mm); n_D^{20} 1.4512; d_4^{20} 1.0812.

Found %: C 47.09; 47.08; H 8.30; 8.30

$C_{10}H_{21}O_5P$. Calculated %: C 47.61; H 8.32

Dipropyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (10 g) was added to a mixture of 6.8 g of pyridine, 5.2 g of absolute propyl alcohol, and 100 ml of dry benzene. The product, amounting to 9.7 g (80%), had b.p. 140° (2 mm); n_D^{20} 1.4510; d_4^{20} 1.0470.

Found %: C 51.34; 51.75; H 9.00; 9.25

$C_{12}H_{25}O_5P$. Calculated %: C 51.42; H 8.92

Diisopropyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}i)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (15 g) was added to a mixture of 8 g of isopropyl alcohol and 11 g of pyridine. Vacuum fractionation yielded 13 g (72%) of product, b.p. 125° (2 mm); n_D^{20} 1.4452; d_4^{20} 1.0341.

Found %: C 51.39; 51.76; H 9.10; 9.02

$C_{12}H_{25}O_5P$. Calculated %: C 51.42; H 8.92

Diisobutyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}i)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (11.65 g) was added to a mixture of 7.5 g of absolute isobutyl alcohol and 8 g of pyridine. The product, amounting to 12.6 g (82%), had b.p. 143° (2 mm); n_D^{20} 1.4492; d_4^{20} 1.0159.

Found %: P 9.89; 9.97

$C_{14}H_{29}O_5P$. Calculated %: P 10.06

Diallyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_3H_5)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (10 g) was added to a cooled mixture of 5 g of absolute allyl alcohol, 7 g of pyridine, and 70 ml of dry benzene. Fractional distillation yielded 9 g (67%) of product, b.p. 138.5° (2 mm); n_D^{20} 1.4702; d_4^{20} 1.0854.

Found %: C 52.10; 51.83; H 7.86; 8.04

$C_{12}H_{21}O_5P$. Calculated %: C 52.17; H 7.60

Diheptyl 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OC_7H_{15}\text{-}n)_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (11.65 g) was added to a mixture of 11.7 g of absolute heptyl alcohol, 8 g of pyridine, and 110 ml of benzene. The product (17 g) had b.p. 200° (1 mm); n_D^{20} 1.4546; d_4^{20} 0.9745.

Found %: C 61.64; 61.79; H 10.52; 10.53; P 7.86; 7.67;

$C_{18}H_{41}O_5P$. Calculated %: C 61.22; H 10.45; P 7.90

Bis(2-methoxyethyl) 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH-CH_2-OCH_3)_2$. Reaction between 11.65 g of 2-(2-ethoxyethoxy)vinylphosphonic dichloride, 7 g of 2-methoxyethanol, and 8 g of pyridine in 100 ml of benzene yielded, after vacuum fractionation, 13.2 g (84%) of product, b.p. 163° (1 mm); n_D^{20} 1.4602; d_4^{20} 1.1279.

Found %: P 9.57; 9.67

$C_{12}H_{25}O_7P$. Calculated %: P 9.93

Bis(2-ethoxyethyl) 2-(2-Ethoxyethoxy)vinylphosphonate $C_2H_5-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$. Reaction between 8 g of 2-ethoxyethanol, 7 g of pyridine, and 10 g of 2-(2-ethoxyethoxy)vinylphosphonic dichloride yielded 12 g (86%) of product, b.p. 180° (1 mm); n_D^{20} 1.4565; d_4^{20} 1.0917.

Found %: C 49.55; 49.42; H 8.68; 8.90

$C_{14}H_{29}O_6P$. Calculated %: C 49.41; H 8.52

2-(2-Butoxyethoxy)vinylphosphonic Esters

Dimethyl 2-(2-Butoxyethoxy)vinylphosphonate $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OCH_3)_2$. Reaction between 2.5 g of absolute methanol, 6.2 g of pyridine, and 10 g of 2-(2-butoxyethoxy)vinylphosphonic dichloride yielded 7.4 g (77%) of product, b.p. 132° (1 mm); n_D^{20} 1.4565; d_4^{20} 1.1100.

Found %: C 47.41; 47.61; H 8.41; 8.61

$C_{10}H_{21}O_5P$. Calculated %: C 47.61; H 8.33

Diethyl 2-(2-Butoxyethoxy)vinylphosphonate $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_2H_5)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (13.5 g) was added with stirring and cooling to a mixture of 4.8 g of absolute ethanol, 7 g of pyridine, and 80 ml of dry benzene. The product, amounting to 11.5 g (79%), had b.p. 155° (2 mm); n_D^{20} 1.4519; d_4^{20} 1.0815.

Found %: C 51.86; 51.82; H 9.12; 9.23

$C_{12}H_{25}O_5P$. Calculated %: C 51.42; H 8.90

Dipropyl 2-(2-Butoxyethoxy)vinylphosphonate n-$C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_3H_7\text{-}n)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (10 g) was added to a cooled mixture of 4.6 g of absolute propyl alcohol, 6.2 g of pyridine, and 100 ml of dry benzene. The product, amounting to 9.5 g (83%), had b.p. 163° (2 mm); n_D^{20} 1.4529; d_4^{20} 1.0199.

Found %: C 54.48; 54.68; H 9.72; 9.74; P 10.58; 10.35

$C_{14}H_{29}O_5P$. Calculated %: C 54.54; H 9.41; P 10.06

Dibutyl 2-(2-Butoxyethoxy)vinylphosphonate n-$C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}n)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (12 g) was added to a mixture of 6.7 g of absolute butyl alcohol and 8 g of pyridine. The product, amounting to 13.5 g (88%), had b.p. 180° (2 mm); n_D^{20} 1.4532; d_4^{20} 1.0008.

Found %: C 56.90; 57.14; H 10.68; 10.04; P 8.86; 9.17

$C_{16}H_{33}O_5P$. Calculated %: C 57.14; H 9.82 P 9.22

Diisobutyl 2-(2-Butoxyethoxy)vinylphosphonate n-$C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_4H_9\text{-}i)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (13.5 g) was added to a mixture of 7.5 g of absolute isobutyl alcohol, 8 g of pyridine, and 75 ml of benzene. The product, amounting to 14.2 g (83%), had b.p. 172° (2 mm); n_D^{20} 1.4512; d_4^{20} 1.0002.

Found %: C 57.33; 57.28; H 10.21; 10.20; P 8.71; 8.90

$C_{16}H_{33}O_5P$. Calculated %: C 57.14 H 9.82 P 9.22

Diallyl 2-(2-Butoxyethoxy)vinylphosphonate n-$C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_3H_5)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (10 g) was added to a cooled mixture of 4.5 g of absolute allyl alcohol, 6.5 g of pyridine, and 120 ml of dry benzene. The product, amounting to 8.2 g (72%), had b.p. 152° (1 mm); n_D^{20} 1.4680; d_4^{20} 1.0530.

Found %: C 55.32; 55.48; H 8.39; 8.35; P 9.79; 9.88

$C_{14}H_{25}O_5P$. Calculated %: C 55.26; H 8.22; P 10.19

Dihexyl 2-(2-Butoxyethoxy)vinylphosphonate n-$C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (10 g) was added to a mixture of 8 g of absolute hexyl alcohol, 7.8 g of pyridine, and 100 ml of benzene. The product, amounting to 12.7 g (85%), had b.p. 202° (2 mm); n_D^{20} 1.4550; d_4^{20} 0.9734.

Found %: C 60.92; 61.02; H 10.75; 10.82

$C_{20}H_{41}O_5P$. Calculated %: C 61.22; H 10.45

Diheptyl 2-(2-Butoxyethoxy)vinylphosphonate n-$C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OC_7H_{15}\text{-}n)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (13.1 g) was added to a mixture of 11.8 g of absolute heptyl alcohol, 8 g of pyridine, and 85 ml of dry benzene. The product, amounting to 18.6 g (89%), had b.p. 207° (1 mm); n_D^{20} 1.4553; d_4^{20} 0.9644.

Found %: C 63.10; 63.10; H 10.75; 10.71; P 7.53; 7.55

$C_{22}H_{45}O_5P$. Calculated %: C 62.85; H 10.70; P 7.32

Bis(2-ethoxyethyl) 2-(2-Butoxyethoxy)vinylphosphonate n-$C_4H_9-O-CH_2-CH_2-O-CH=CHPO(OCH_2-CH_2-O-C_2H_5)_2$. 2-(2-Butoxyethoxy)vinylphosphonic dichloride (13.5 g) was added to a mixture of 9 g of 2-ethoxyethanol, 8 g of pyridine, and 100 ml of dry benzene. The product, amounting to 16.5 g (87%), had b.p. 193° (2 mm); n_D^{20} 1.4561; d_4^{20} 1.0643.

Found %: C 52.00; 51.77; H 9.29; 9.32; P 8.77; 8.71

$C_{16}H_{33}O_7P$. Calculated %: C 52.18; H 8.96; P 8.42

SUMMARY

Twenty-nine diesters of 2-(2-methoxyethoxy)-, 2-(2-ethoxyethoxy)-, and 2-(2-butoxyethoxy)-vinylphosphonic acids have been prepared and characterized.

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 12. BISDIALKYLAMIDES OF 2-(2-ALKOXYETHOXY)VINYLPHOSPHONIC ACIDS

K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

When dialkylamines react with 2-(2-alkoxyethoxy)vinylphosphonic dichlorides, bisdialkylamides of 2-(2-alkoxyethoxy)vinylphosphonic acids are formed in almost quantitative yield.

We have prepared and characterized the bisdimethylamides, bisdiethylamides, bisdipropylamides, bisdibutylamides, and dipiperidides of 2-(2-methoxyethoxy)-, 2-(2-ethoxyethoxy)-, and 2-(2-butoxyethoxy)vinylphosphonic acids. These substances are liquids which can be readily distilled under reduced pressure. They are soluble in all organic solvents, and some of them are soluble also in water. All bisdialkylamides of 2-(2-alkoxyethoxy)vinylphosphonic acids are stable to storage.

Their constants are given in Table 1.

TABLE 1

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Yield (%)
$CH_3-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$	144 (2)	1.4808	1.0879	56
$CH_3-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$	153 (2)	1.4765	1.0191	59
$CH_3-O-CH_2-CH_2-O-CH=CHPO[N(C_3H_7\text{-}n)_2]_2$	130 (1)	1.4733	0.9932	65
$CH_3-O-CH_2-CH_2-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$	183 (1)	1.4710	0.9741	75
$CH_3-O-CH_2-CH_2-O-CH=CHPO[N(CH_2-CH_2)_2CH_2]_2$	187 (1)	1.5101	1.1026	84
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$	143 (2)	1.4770	1.0545	72
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$	146 (1)	1.4749	1.0108	78
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_3H_7\text{-}n)_2]_2$	163 (2)	1.4721	0.9822	83
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$	180 (1)	1.4705	0.9579	93
$C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(CH_2-CH_2)_2CH_2]_2$	185 (2)	1.5062	1.0851	96
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$	175 (2)	1.4758	1.0274	71
$n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$	179 (2)	1.4730	0.9948	87

EXPERIMENTAL

Bisdimethylamide of 2-(2-Methoxyethoxy)vinylphosphonic Acid $CH_3-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$. A solution of 13 g of dimethylamine in 100 ml of petroleum ether was poured into a three-necked flask, fitted with stirrer and reflux condenser and cooled with ice and salt. The solution was stirred while 15.8 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride was added. On the next day, after the mixture had been heated for two hours at 30° in a water bath, dimethylamine hydrochloride was filtered off, and the filtrate was treated with 10% sodium carbonate solution and dried over potassium carbonate. Vacuum fractionation yielded 9.5 g (56%) of a substance having b.p. 144° (2 mm); n_D^{21} 1.4808; d_4^{20} 1.0879.

Found %: P 12.97; 13.04

$C_9H_{21}O_3PN_2$. Calculated %: P 13.26

The other bisdialkylamides were prepared under conditions similar to those described above.

Bisdiethylamide of 2-(2-Methoxyethoxy)vinylphosphonic Acid $CH_3-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (10.85 g) was added to a solution of 15 g of diethylamine in 120 ml of a mixture of petroleum ether and benzene. The product, amounting to 8.6 g, had b.p. 153° (2 mm); n_D^{20} 1.4765; d_4^{20} 1.0191.

Found %: P 10.60; 10.32

$C_{13}H_{29}O_3PN_2$. Calculated %: P 10.61

Bisdipropylamide of 2-(2-Methoxyethoxy)vinylphosphonic Acid $CH_3-O-CH_2-CH_2-O-CH=CHPO[N(C_3H_7\text{-}n)_2]_2$. Reaction of 8.13 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride with 16 g of dipropylamine yielded 8.5 g (65%) of a substance having b.p. 160° (1 mm); n_D^{20} 1.4733; d_4^{20} 0.9932.

Found %: P 8.81; 8.98

$C_{17}H_{37}O_3PN_2$. Calculated %: P 8.90

Bisdibutylamide of 2-(2-Methoxyethoxy)vinylphosphonic Acid $CH_3-O-CH_2-CH_2-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$. 2-(2-Methoxyethoxy)vinylphosphonic dichloride (10.85 g) was added to 30 g of dibutylamine. The product, amounting to 15 g (75%), had b.p. 183° (1 mm); n_D^{20} 1.4710; d_4^{20} 0.9741.

Found %: N 6.64; 6.65

$C_{21}H_{45}O_2N_2P$. Calculated %: N 6.93

Dipiperidide of 2-(2-Methoxyethoxy)vinylphosphonic Acid $CH_3-O-CH_2-CH_2-O-CH=CHPO\left[N\begin{matrix}CH_2-CH_2\\ \diagdown\quad\diagup\\ CH_2-CH_2\end{matrix}CH_2\right]_2$. Piperidine (20 g) was added to 10.85 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride. The product, amounting to 14.4 g (84%), had b.p. 187° (1 mm); n_D^{20} 1.5101; d_4^{20} 1.1026.

Found %: P 9.47; 9.53

$C_{15}H_{27}O_3PN_2$. Calculated %: P 9.80

Bisdimethylamide of 2-(2-Ethoxyethoxy)vinylphosphonic Acid $C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$. Dimethylamine (9 g) was added to an ice-cooled mixture of petroleum ether and benzene. To this mixture, 10.65 g of 2-(2-ethoxyethoxy)vinylphosphonic dichloride was added. The product, amounting to 8.2 g (72%), had b.p. 143° (2 mm); n_D^{20} 1.4770; d_4^{20} 1.0545.

Found %: N 11.20; 10.59

$C_{10}H_{23}O_3PN_2$. Calculated %: N 11.20

Bisdiethylamide of 2-(2-Ethoxyethoxy)vinylphosphonic Acid $C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (10 g) was added to 12.5 g of diethylamine. The product, amounting to 10 g (78%), had b.p. 146° (2 mm); n_D^{20} 1.4749; d_4^{20} 1.0108.

Found %: N 8.96; 9.13

$C_{14}H_{31}O_3PN_2$. Calculated %: N 9.15

Bisdipropylamide of 2-(2-Ethoxyethoxy)vinylphosphonic Acid $C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_3H_7\text{-}n)_2]_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (10 g) was added to 18 g of dipropylamine. The product, amounting to 12.8 g (83%), had b.p. 163° (2 mm); n_D^{20} 1.4721; d_4^{20} 0.9822.

Found %: N 7.61; 7.65

$C_{18}H_{39}O_3PN_2$. Calculated %: N 7.73

Bisdibutylamide of 2-(2-Ethoxyethoxy)vinylphosphonic Acid $C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$. 2-(2-Ethoxyethoxy)vinylphosphonic dichloride (10 g) was added to 23 g of dibutylamine. The product, amounting to 16.5 g (93%), had b.p. 180° (1 mm); n_D^{20} 1.4705; d_4^{20} 0.9579.

Found %: N 6.86; 6.63

$C_{22}H_{47}O_3PN_2$. Calculated %: N 6.69

Di[peridide] of 2-(2-Ethoxyethoxy)vinylphosphonic Acid $C_2H_5-O-CH_2-CH_2-O-CH=CHPO\left[N\begin{smallmatrix}CH_2-CH_2\\ \\ CH_2-CH_2\end{smallmatrix}CH_2\right]_2$. Reaction between 10 g of 2-(2-ethoxyethoxy)vinylphosphonic dichloride and 15 g of piperidine yielded 13.5 g (96%) of a substance having b.p. 185° (1 mm); n_D^{20} 1.5062; d_4^{20} 1.0851.

Found %: N 8.58; 8.77

$C_{16}H_{31}O_3PN_2$. Calculated %: N 8.48

Bisdimethylamide of 2-(2-Butoxyethoxy)vinylphosphonic Acid $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO[N(CH_3)_2]_2$. Dimethylamine (9 g) was added to an ice-cooled mixture of petroleum ether and benzene, and then, gradually and with stirring, 12 g of 2-(2-butoxyethoxy)vinylphosphonic dichloride was added. The product, amounting to 9 g (71%), had b.p. 175° (2mm); n_D^{20} 1.4758; d_4^{20} 1.0274.

Found %: P 10.82; 11.02

$C_{12}H_{27}O_3PN_2$. Calculated %: P 11.15

Bis[diethylamide] of 2-(2-Butoxyethoxy)vinylphosphonic Acid $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$. Reaction of 13.5 g of 2-(2-butoxyethoxy)vinylphosphonic dichloride with 15 g of diethylamine yielded 15 g (87%) of a substance having b.p. 179° (2 mm); n_D^{20} 1.4730; d_4^{20} 0.9948.

Found %: P 9.20; 9.21

$C_{16}H_{35}O_3PN_2$. Calculated %: P 9.28

SUMMARY

Twelve bis[dialkylamides] of 2-(2-alkoxyethoxy)vinylphosphonic acids have been synthesized and characterized.

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SYNTHESIS OF ALKOXYBROMOTITANIUMS AND ALKOXYCHLOROPOLYTITANOXANES

A. N. Nesmeyanov, E. M. Brainina, and R. Kh. Freidlina

Several methods have been proposed in recent years for the synthesis of alkoxychlorotitaniums, and, as a result, compounds of this type containing one, two, and three chlorine atoms in their molecules have become readily accessible [1-3, 9, 11, 13-16]. The only alkoxybromotitaniums known are dialkoxydibromotitaniums obtained in the form of double compounds with alcohols: $(RO)_2TiBr_2 \cdot ROH$. These compounds were prepared by two of the present authors in collaboration with Nogina [1] by the action of bromine on alkyl orthotitanates.

A few papers and patents have been devoted to the preparation and study of organopolytitanoxanes [4-8, 12, 17]. It was found that polymeric compounds are formed in the thermal decomposition of alkyl orthotitanates [4-6, 12]. In the thermal decomposition of butyl orthotitanate, the products, apart from titanium-containing polymer, include butyl alcohol and butyraldehyde according to one investigation [6], and butyl alcohol and butene, according to others [5, 12]. The thermal decomposition of alkyl orthotitanates cannot be regarded as a convenient method of synthesizing polytitanoxanes, since the reaction requires long heating at a high temperature, and is not controllable [5].

Another method for the preparation of compounds containing the polytitanoxane chain is the action of water on alkyl orthotitanates [6-8, 17]. It is reported [7, 17] that linear polymers are formed by the action of water on butyl orthotitanate so long as the molar ratio of the water and ester taken for reaction is not greater than unity. In the same papers it is stated that with such proportions of water and ester the polymers formed have a medium degree of polymerization (estimated from the titanium content of the polymer) corresponding to that calculated from the equation:

$$n(RO)_4Ti + (n-1)\,H_2O \longrightarrow (RO)_{2n+2}Ti_nO_{n-1} + 2(n-1)\,ROH.$$

According to our results [8], by reaction of one molecular proportion of water with two molecular proportions of ethyl orthotitanate, not hexaethoxydititanoxane $(C_2H_5O)_6Ti_2O$, (in accordance with the equation), but octaethoxytrititanoxane $(C_2H_5O)_8Ti_3O_2$, is formed.

The investigation of polyalkoxypolytitanoxanes is rendered difficult by the fact that these substances are usually highly viscous liquids, which decompose when distilled under reduced pressure (2-3 mm). The purification of these compounds by other methods is rendered difficult by the extreme readiness with which they undergo hydrolysis. Molecular weight determinations on these substances do not usually yield unequivocal results, since polyalkoxypolytitanoxanes are associated in solution and the degree of association depends on the concentration. It is characteristic of these compounds that each repeating unit of the chain, which contains one titanium atom, is multifunctional, a fact that makes it difficult to establish the structures of these compounds.

At the present stage of development in this field, special interest is presented by polyalkoxypolytitanoxanes containing only a few titanium atoms in the polytitanoxane chain, since these compounds can be more readily isolated and identified. Up to the present, apart from octaethoxytrititanoxane, described by us [8], hexabutoxydititanoxane $(C_4H_9O)_6Ti_2O$ [12, 7] and hexaallyloxydititanoxane $(C_3H_5O)_6Ti_2O$ [6] have been described. Hexabutoxydititanoxane was prepared both by the thermal decomposition of butyl orthotitanate and by the action of water on this ester [12]. This compound was not purified in any way; its composition was established merely by analysis for titanium.

In the thermal decomposition of allyl orthotitanate, a residue was obtained which roughly corresponded in analysis to hexaallyloxydititanoxane; the experimentally determined molecular weight differed greatly from the calculated value [6].

No organopolytitanoxanes containing halogen have been described.

Octaethoxytrititanoxane $(C_2H_5O)_8Ti_3O_2$, which we prepared by the hydrolysis of ethyl orthotitanate, is a crystalline substance and can be purified by recrystallization from alcohol or benzene; its composition was established by analysis for carbon, hydrogen, and titanium [8]. The determination of the molecular weight of this compound in fairly dilute benzene solution by the cryoscopic method gave a value close to the calculated value [8].

In the present paper we describe the conversion of octaethoxytrititanoxane into other octaalkoxytrititanoxanes by transesterification:

$$(C_2H_5O)_8Ti_3O_2 + 8\ ROH \rightarrow (RO)_8Ti_3O_2 + 8C_2H_5OH,$$

in which R = n-C_4H_9 and n-C_6H_{13}.

The resulting octabutoxy- and octahexyloxy-trititanoxanes were found to be viscous liquids. When attempts were made to distil them at 2-5 mm, butyl and hexyl orthotitanates were obtained, respectively. It was further shown that equimolecular amounts of octaethoxytrititanoxane and acetyl chloride react together with formation of a chloroheptaethoxytrititanoxane and ethyl acetate, in accordance with the equation (see also [14]):

$$(C_2H_5O)_8Ti_3O_2 + CH_3COCl \rightarrow (C_2H_5O)_7Ti_3O_2Cl + CH_3CO_2C_2H_5.$$

When octaalkoxytrititanoxanes reacted with two molecular proportions of acetyl chloride, hexaalkoxydichlorotrititanoxanes and alkyl acetates were obtained, in accordance with the equation:

$$(RO)_8Ti_3O_2 + 2\ CH_3COCl \rightarrow (RO)_6Ti_3O_2Cl_2 + 2CH_3CO_2R,$$

in which R = C_2H_5, n-C_4H_9, n-C_6H_{13}.

Of all of the chlorotrititanoxanes prepared, only compounds containing ethoxy groups were found to be solids, the remainder being viscous liquids. The positions of the chlorines in these compounds were not investigated. When hexaalkoxydichlorotitanoxanes were vacuum-distilled, the corresponding trialkoxychlorotitaniums were obtained.

We have studied also the reaction of disproportionation in reverse for the purpose of the synthesis of alkoxybromotitaniums. In the reaction of ethyl orthotitanate with titanium tetrabromide at room temperature we obtained, depending on the proportion of reactants, different bromoethoxytitaniums in accordance with the equations:

$$(RO)_4Ti + TiBr_4 \rightarrow 2(RO)_2TiBr_2$$

$$(RO)_4Ti + 3TiBr_4 \rightarrow 4ROTiBr_3.$$

This reaction, like that between an alkyl orthotitanate and titanium tetrachloride [2, 3], can be carried out in presence of the calculated amount of piperidine, when crystalline double compounds of formula:

$$(RO)_nTiBr_{4-n}\ C_5H_{10}NH,$$

are formed between the bromoethoxytitanium and piperidine (n = 1 and 2).

These double compounds are readily purified by recrystallization.

EXPERIMENTAL

All experiments were carried out under conditions that precluded access of atmospheric moisture; all substances were carefully dried.

Octaethoxytrititanoxane • $(C_2H_5O)_8Ti_3O_2$. A solution of 1.31 g (0.073 mole) of water in 10 ml of absolute alcohol was added gradually with vigorous stirring to a solution of 33.7 g (0.147 mole) of ethyl orthotitanate in 15 ml of absolute alcohol. The reaction mixture was then heated to the boil, when most of the precipitate that had formed was dissolved. The hot solution was filtered from the small amount of insoluble residue. The filtrate was

• We have already given a brief description of the preparation of this compound and some of its properties [8].

cooled and yielded 14.6 g of precipitate, which corresponds to a 75% yield, on the basis of the amount of water taken for reaction. The analysis of the non-crystallized product was closely in accord with that calculated for octaethoxytrititanoxane. The product was recrystallized from the least possible amount (7 ml) of alcohol and again analyzed.

Found %: C 35.95; 35.95; H 7.57; 7.56; Ti 26.45; 26.54
$(C_2H_5O)_8Ti_3O_2$. Calculated %: C 35.82; H 7.52; Ti 26.81

The substance melts in a sealed capillary over a wide range of temperature (~ 78-85°). Careful evaporation of the mother liquor gave still a little more octaethoxytrititanoxane; under these conditions, therefore, no polymers differing in degree of polymerization are formed.

Octabutoxytrititanoxane (n-$C_4H_9O)_8Ti_3O_2$. A solution of 10.7 g of recrystallized octaethoxytrititanoxane in 20 ml of butyl alcohol was heated for two hours. The alcohols present were then distilled off. More butyl alcohol was added, and the operation was repeated, when it was found that pure butyl alcohol came over. The butyl alcohol was distilled off under reduced pressure. The residual viscous liquid was dissolved in petroleum ether, and the solution was filtered. Attempts to crystallize the substance from this solution were not successful, and the solvent was therefore distilled off, the residue being carefully freed from volatile substances by heating at 90° under a residual pressure of 3 mm for 40 minutes. Octabutoxytrititanoxane is a light-yellow viscous liquid. It is hygroscopic, and it readily undergoes hydrolysis.

Found %: C 50.63; 50.80; 50.71; H 9.74; 9.70; 9.60; Ti 19.13; 19.04; 18.91
$(C_4H_9O_4)Ti_2O_2$. Calculated %: C 50.51; H 9.70; Ti 18.90

When octabutoxytrititanoxane (19 g) was heated in an oil bath at 200-220°, butyl orthotitanate distilled off (the temperature in the vapor was 149-150° at a residual pressure of 2-3 mm), the amount collected being 5.2 g. Solid polymer remained behind in the distilling flask. When redistilled, the butyl orthotitanate boiled at 167-167.5° (5 mm).

Found %: C 55.86; 55.94; H 10.69; 10.82; Ti 13.98; 14.19
$(C_4H_9O)_4Ti$. Calculated %: C 56.45; H 10.66; Ti 14.08

For $(C_4H_9O)_4Ti$ the literature [9] gives b.p 160-162° (2 mm).

Octahexyloxytrititanoxane (n-$C_6H_{13}O)_8Ti_3O_2$. The procedure was the same as in the preceding experiment. Reaction between 4.3 g of octaethoxytrititanoxane and 55 ml of hexyl alcohol gave a quantitative yield of liquid octahexyloxytrititanoxane.

Found %: C 58.48; 58.76; H 10.54; 10.59; Ti 14.60; 14.36
$(C_6H_{13}O)_8Ti_3O_2$. Calculated %: C 58.51; H 10.65; Ti 14.60

When 21.1 g of octahexyloxytrititanoxane was heated in a water bath at 250-260°, hexyl orthotitanate distilled off (the temperature in the vapor was 203-205° at a residual pressure of 2.5 mm), the amount collected being 10.7 g. After redistillation the hexyl orthotitanate boiled at 199° (2 mm); it had n_D^{18} 1.4840.

Found %: C 63.61; 64.07; H 11.62; 11.75; Ti 10.29; 10.30
$(C_6H_{13}O)_4Ti$. Calculated %: C 63.66; H 11.60; Ti 10.59

For (n-$C_6H_{13}O)_4Ti$ the literature [10] gives b.p. 201-204° (2 mm), n_D^{18} 1.4830.

Chloroheptaethoxytrititanoxane($C_2H_5O)_7Ti_3O_2Cl$. A solution of 0.78 g (0.01 mole) of acetyl chloride in 3 ml of petroleum ether was added to a cooled solution of 5.36 g (0.01 mole) of octaethoxytrititanoxane in 5 ml of petroleum ether. The reaction mixture was heated for two hours at 70-75°, cooled, and filtered from suspended matter. Solvent and ethyl acetate was distilled from the filtrate. The solid product was very readily soluble in petroleum ether. Attempts to recrystallize it from this solvent with cooling to − 70° were not successful. The product was freed from volatile impurities by heating it for two hours at 50° at a residual pressure of 2 mm. When heated in a sealed capillary, the substance melted over a wide temperature range.

Found %: C 32.24; 32.24; H 6.83; 6.64; Ti 26.79; 26.73
$(C_2H_5O)_7Ti_3O_2Cl$. Calculated %: C 31.91; H 6.68; Ti 27.30

Dichlorohexaethoxytrititanoxane ($C_2H_5O)_6Ti_3O_2Cl_2$. The procedure was as in the preceding experiment. Treatment of a solution of 4.8 g (0.0089 mole) of octaethoxytrititanoxane in 5 ml of petroleum ether with a solution of 1.4 g (0.0178 mole) of acetyl chloride in 3 ml of petroleum ether yielded 3.7 g (which corresponds to a

quantitative yield) of solid dichlorohexaethoxytrititanoxane.

Found %: C 28.20; 27.96; H 6.10; 6.09; Ti 27.43; 27.61
$(C_2H_5O)_6Ti_3O_3Cl_2$. Calculated %: C 27.87; H 5.83; Ti 27.81

The product was recrystallized from petroleum ether and filtered off through a funnel cooled with a mixture of acetone and dry ice. The residue on the filter was dissolved in a new portion of petroleum ether, and solvent was then removed completely under reduced pressure.

Found %: Cl 14.19; 14.20
Calculated %: Cl 13.74

Hexabutoxydichlorotrititanoxane (n-$C_4H_9O)_6Ti_3O_3Cl_2$. The procedure was as in the preceding experiments. Treatment of a solution of 11.45 g (0.015 mole) of octabutoxytrititanoxane in 15 ml of petroleum ether with a solution of 2.36 g (0.030) mole) of acetyl chloride in 5 ml of benzene gave 9.5 g (92%) of hexabutoxydichlorotrititanoxane, in the form of a viscous liquid.

Found %: C 41.98; 41.86; H 7.91; 7.93; Cl 10.26; 10.59; Ti 20.70; 20.81
$(C_4H_9O)_6Ti_3O_3Cl_2$. Calculated %: C 42.04; H 7.94 Cl 10.35; Ti 20.98

When 4.33 g of the product was vacuum-distilled, some liquid (1.83 g) came over at 145-146° (1 mm). Solid polymer remained behind in the distilling flask. Redistillation of the distillate yielded tributoxychlorotitanium, b.p. 156.5° (2.5 mm); n_D^{20} 1.5192.

Found %: C 47.51; 47.54; H 8.96; 9.00; Ti 15.55; 16.09
$(C_4H_9O)_3TiCl$. Calculated %: C 47.61; H 8.99 Ti 15.82

For tributoxychlorotitanium the literature [11] gives b.p. 154-155° (2 mm); n_D^{20} 1.5169.

Dichlorohexahexyloxytrititanoxane (n-$C_6H_{13}O)_6Ti_3O_3Cl_2$. The procedure was as in the preceding experiments. Treatment of a solution of 14.82 g (0.015 mole) of octahexyloxytrititanoxane in 10 ml of petroleum ether with a solution of 2.36 g (0.030 mole) of acetyl chloride in 3 ml of petroleum ether yielded liquid dichlorohexahexyloxytrititanoxane.

Found %: C 50.54; 50.39; H 9.18; 9.21; Ti 16.91; 16.99
$(C_6H_{13}O)_6Ti_3O_3Cl_2$. Calculated %: C 50.63; H 9.21; Ti 16.84

When 10 g of the product was distilled, a substance boiling at 178° (1 mm) came over. Solid polymer (2 g) remained behind in the flask. Redistillation of the distillate yielded chlorotrihexyloxytitanium, b.p. 198-201° (2 mm); n_D^{20} 1.5060.

Found %: C 55.16; 55.20; H 10.14; 10.10; Ti 12.02; 11.80
$(C_6H_{13}O)_3TiCl$. Calculated %: C 55.88; H 10.16; Ti 12.38

For chlorotrihexyloxytitanium the literature [11] gives b.p. 182-182.5° (1 mm); n_D^{20} 1.5050.

Dibromodiethoxytitanium $(C_2H_5O)_2TiBr_2$. A solution of 1.84 g (0.005 mole) of freshly distilled titanium tetrabromide in 5 ml of benzene was added to a solution of 1.14 g (0.005 mole) of ethyl orthotitanate in 6 ml of a mixture of equal volumes of benzene and petroleum ether. The reaction mixture was cooled at −10 to −15° for a long time, and a precipitate finally formed (2.29 g, i.e. 79%). It was recrystallized from benzene and dried in a current of dry air. When heated in a sealed capillary, the substance melted with decomposition over the range 47-50° with formation of a red liquid.

Found %: C 16.36; 16.21; H 3.74; 3.62; Ti 16.38; 16.44
$(C_2H_5O)_2TiBr_2$. Calculated %: C 16.12; H 3.38 Ti 16.09

Tribromoethoxytitanium $C_2H_5OTiBr_3$. The procedure was as in the preceding experiment. A solution of 11.02 g (0.03 mole) of titanium tetrabromide in 5 ml of benzene was treated with a solution of 2.28 g (0.01 mole) of ethyl orthotitanate in 3 ml of petroleum ether, the resulting mixture being cooled for one day. The precipitate that then formed amounted to 5.8 g (45%). It was found possible to obtain a little more of this compound by careful evaporation of the mother liquor. The substance was recrystallized from a mixture of benzene and petroleum ether.

Found %: C 7.96; 7.99; H 1.87; 1.73; Ti 14.41; 14.20

$(C_2H_5O)TiBr_3$. Calculated %: C 7.23; H 1.51; Ti 14.43

When heated in a sealed capillary, the substance melted over an extended range.

Double Compound formed by Dibromodiethoxytitanium with Piperidine $(C_2H_5O)_2TiBr_2C_5H_{11}NH$. A solution of 1.70 g (0.02 mole) of piperidine in 3 ml of benzene was added to a cooled solution of 2.28 g (0.01 mole) of ethyl orthotitanate in 3 ml of petroleum ether. A solution of 3.67 g (0.01 mole) of titanium tetrabromide in 5 ml of benzene was then added dropwise to the resulting mixture, when a light-yellow precipitate formed. The mixture was set aside overnight, and the precipitate was then filtered off, washed with petroleum ether, and dried (6.13 g, i.e. 80%). It was recrystallized from benzene.

Found %: C 29.06; 28.96; H 5.72; 5.52; Ti 12.31; 12.27; N 3.48; 3.44

$(C_2H_5O)_2TiBr_2C_5H_{11}N$. Calculated %: C 28.20; H 5.53; Ti 12.51; N 3.65

Double Compound formed by Bromotriethoxytitanium with Piperidine $(C_2H_5O)_3TiBrC_5H_{10}NH$. The procedure was as in the preceding experiment. Reaction of 6.48 g (0.03 mole) of ethyl orthotitanate, 3.40 g (0.04 mole) of piperidine, and 3.67 g (0.01 mole) of titanium tetrabromide in the least possible volume of a mixture of benzene and petroleum ether yielded 10.48 g (75%) of the double compound. The substance was recrystallized from a mixture of benzene and petroleum ether.

Found %: C 37.89; 37.85; H 7.38; 7.40; Br 22.94; 23.85; Ti 13.70; 13.75; N 4.02; 3.87

$(C_2H_5O)_3TiBrC_5H_{10}NH$. Calculated %: C 37.93; H 7.52; Br 23.06; Ti 13.76; N 4.02

SUMMARY

1. By the transesterification of octaethoxytrititanoxane, octabutoxy- and octahexyloxy-trititanoxanes $(n\text{-}C_4H_9O)_8Ti_3O_2$ and $(n\text{-}C_6H_{13}O)_8Ti_3O_2$ were prepared.

2. Treatment of octaalkoxytrititanoxanes with acetyl chloride yielded compounds of formula:

$(C_2H_5O)_7Ti_3O_2Cl$, $(C_2H_5O)_6Ti_3O_2Cl_2$.
$(n\text{-}C_4H_9O)_6Ti_3O_2Cl_2$, $(n\text{-}C_6H_{13}O)_6Ti_3O_2Cl_2$.

3. Hexabutoxydichloro- and dichlorohexahexyloxy-trititanoxanes decomposed when heated under reduced pressure with formation of the corresponding trialkoxychlorotitaniums and polymers.

4. Treatment of ethyl orthotitanate with titanium tetrabromide yielded compounds of formula:

$(C_2H_5O)_2TiBr_2$ and $C_2H_5OTiBr_3$.

5. By reaction of titanium tetrabromide with ethyl orthotitanate in presence of the calculated amount of piperidine, crystalline double compounds having the following formulas were prepared:

$(C_2H_5O)_2TiBr_2 \cdot C_5H_{11}NH$ and $(C_2H_5O)_3TiBr \cdot C_5H_{10}NH$.

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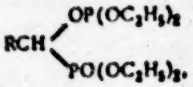
* T.p. = C. B. Translation pagination.

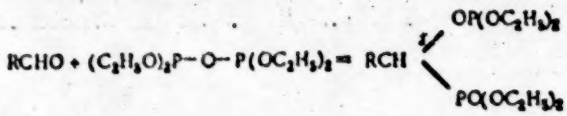
SOME DERIVATIVES OF 1-HYDROXYALKYLPHOSPHONIC ACIDS

P. I. Alimov and O. N. Fedorova

In 1951 we [1] described a method for the synthesis of some derivatives of 1-hydroxyalkylphosphonic acids of general formula

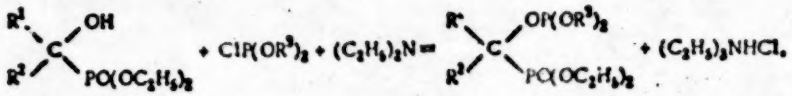


in which R is an aliphatic or aromatic radical. These substances were synthesized by the reaction of tetraethyl pyrophosphite with aldehydes:



The aldehydes used were: butyraldehyde, benzaldehyde, p-tolualdehyde, 2-furaldehyde, and acetaldehyde. An attempt to extend this reaction to ketones was not successful: it was found that pyrophosphorous esters do not react with acetone.

In the present paper we describe the synthesis of organophosphorus compounds of this type by the reaction of dialkyl phosphorochloridites with 1-hydroxyalkylphosphonic esters in presence of triethylamine:



in which R^1 is H or alkyl, and R^2 and R^3 are alkyls. The reaction was carried out in an organic solvent (gasoline, ether) at room temperature, the reaction mixture being finally heated to bring reaction to completion. These derivatives of 1-hydroxyalkylphosphonic acids can be regarded as mixed phosphorous esters, i.e. dialkyl 1-(diethoxyphosphinyl)alkyl phosphites.

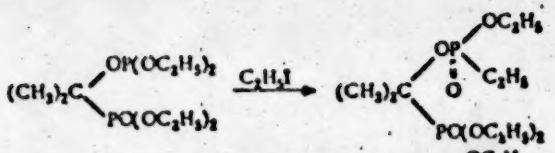
This second method of synthesis became readily accessible when Abramov [2] discovered a simple method for preparing esters of 1-hydroxyalkylphosphonic acids. Whereas the first method was limited to the preparation of compounds of this type from aldehydes and in such a way that all the radicals of the ester groupings were necessarily identical, in the second method ketones can be used as reactants and the radicals of the ester groupings can be the same or different.

We prepared our 1-hydroxyalkylphosphonic esters from diethyl hydrogen phosphite and a carbonyl compound, namely, acetaldehyde, acetone, or 2-butanone. As acid chlorides we used diethyl, dipropyl, and diisobutyl phosphorochloridites.

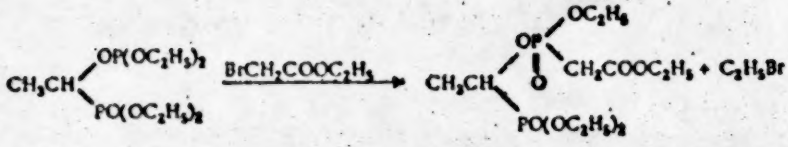
Table 1 gives the formulas, physical constants, and yields of mixed phosphorous esters that we have synthesized by the second method.

The compounds listed in Table 1 are colorless, very mobile liquids having a feeble odor of phosphonic acid derivatives. They are soluble in water and in organic solvents.

Since dialkyl 1-(diethoxyphosphinyl)alkyl phosphites contain one tervalent phosphorus atom attached to ester groupings, they readily undergo isomerization and rearrangement under the action of halo compounds (Arbuzov reaction) with formation of compounds having two quinquevalent phosphorus atoms, for example



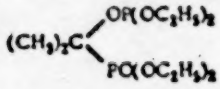
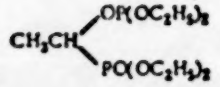
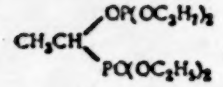
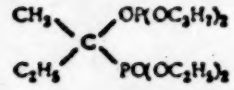
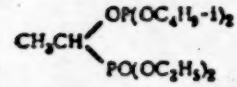
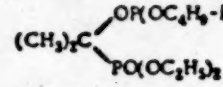
(1)



(2)

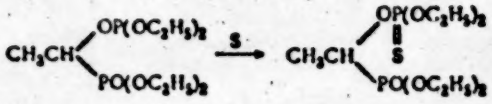
The formulas of substances prepared by this isomerization and rearrangement reaction, together with their physical constants and yields, are given in Table 2.

TABLE 1

Formula	B.p. in °C (p in mm)	n_D^{18}	d_4^{18}	MR		Yield (%)
				Found	Calculated	
	106-107 (0.5)	1.4379	1.0752	77.14	76.98	63.1
	109-110 (1.0)	1.4376	1.0925	72.51	72.37	78.12
	129-130 (1)	1.4395	1.0610	81.89	81.75	50.49
	136.5-138 (1.5)	1.4435	1.057	89.88	90.84	46.65
	128-128.5 (1)	1.4372	1.0345	90.70	90.83	52.25
	126-127 (1)	1.4390	1.0277	95.21	95.46	48.12

The isomerization and rearrangement products of the mixed phosphorous esters are colorless mobile liquids. They have either no odor, or only a very feeble ethereal odor. They are readily soluble in water and in organic solvents.

Sulfur readily adds to dialkyl 1-(diethylphosphinyl)alkyl phosphites with formation of compounds containing two quinquevalent phosphorus atoms, for example:



The formulas, constants, and yields of compounds prepared in this way are given in Table 3.

The organophosphorus compounds listed in Table 3 are colorless mobile liquids having odors characteristic of sulfur compounds. They are sparingly soluble in water, but readily soluble in alcohol and other organic solvents.

TABLE 2

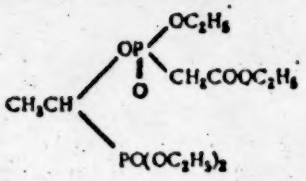
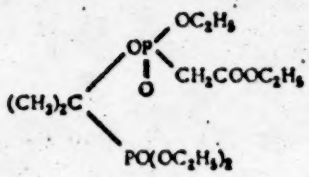
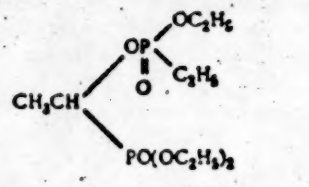
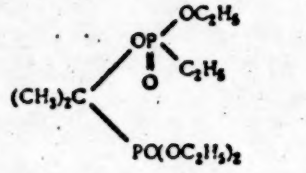
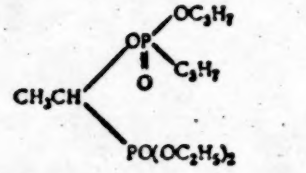
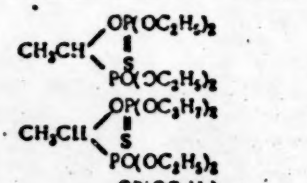
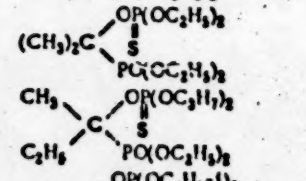
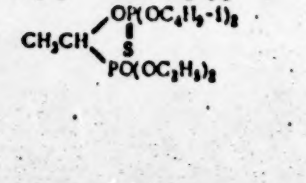
Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		Yield (%)
				Found	Calculated	
	170-171.5 (1)	1.4425	1.1761	81.07	81.15	54.5
	169-170.5 (1)	1.4450	1.1570	86.03	85.62	47.56
	141.5-143 (1)	1.4370	1.1295	70.05	70.11	81.00
	140-141.5(1)	1.4395	1.1165	74.52	74.73	69.59
	140-142 (0.5)	1.4388	1.0879	79.75	79.49	37.5

TABLE 3

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		Yield (%)
				Found	Calculated	
	145-146 (1)	1.4561	1.1528	78.79	78.74	62.72
	156-157 (1)	1.4550	1.1166	87.96	88.12	75.66
	145-146 (1.5)	1.4576	1.1419	83.10	83.35	56.7
	161-162 (1)	1.4598	1.1017	96.92	97.21	36.7
	151-152.5 (1)	1.4525	1.0843	97.12	97.21	65.26

EXPERIMENTAL

Preparation of Dialkyl 1-(Diethoxyphosphinyl)alkyl Phosphites (Table 1)

1. Diethyl 1-(Diethoxyphosphinyl)-1-methylethyl Phosphite. Diethyl phosphorochloridite (15 g) was added at room temperature to a stirred solution of 18.8 g of diethyl 1-hydroxy-1-methylethylphosphonate and 9.7 g of triethylamine in gasoline (b.p. 75-120°). Reaction proceeded with slight evolution of heat, and triethylamine hydrochloride separated. When the whole of the acid chloride had been added, the flask containing the reaction mixture was heated in a glycerol bath at 50-60° for one hour. The mixture was cooled, and the precipitate of triethylamine hydrochloride was filtered off and washed with gasoline. The weight of dry salt was 12.3 g (93.4%), and the weight of reaction product was 30 g. Two distillations of the crude product from an Arbuzov flask yielded a main fraction of b.p. 106-107° (0.5 mm); yield 19.07 g (63.1%); n_D^{20} 1.4379; d_4^{20} 1.0752; found MR 77.14; calculated for $C_{11}H_{25}P_2O_6$ MR 76.98.

Found %: P 19.79; 19.75

$C_{11}H_{25}P_2O_6$. Calculated %: P 19.62

The substance is a colorless mobile liquid having a feeble odor of derivatives of phosphonic acids. It is sparingly soluble in water, but readily soluble in alcohol and gasoline.

2. Diethyl 1-(Diethylphosphinyl)ethyl Phosphite. Reaction was between 18.9 g of diethyl 1-hydroxyethylphosphonate, 10.5 g of diethylamine, and 16.3 g of diethyl phosphorochloridite. The procedure was similar to that of the preceding experiment. Distillation of the crude product yielded 24.5 g (78.12%) of a substance having b.p. 117.5-118.5° (1 mm); n_D^{20} 1.4376; d_4^{20} 1.0925; found MR 72.51; calculated for $C_{10}H_{24}P_2O_6$ MR 72.37.

Found %: P 20.74; 20.62

$C_{10}H_{24}P_2O_6$. Calculated %: P 20.53

3. Dipropyl 1-(Diethoxyphosphinyl)ethyl Phosphite. Reaction was between 16.77 g of diethyl 1-hydroxyethylphosphonate, 9.3 g of diethylamine, and 17 g of dipropyl phosphorochloridite. The reaction was carried out in gasoline solution. Two fractionations of the reaction product from an Arbuzov flask yielded a main fraction amounting to 15 g (50.49%); it had b.p. 129-130° (1 mm); n_D^{20} 1.4395; d_4^{20} 1.0610; found MR 81.89; calculated for $C_{12}H_{28}P_2O_6$ MR 81.75.

Found %: P 19.06; 19.18

$C_{12}H_{28}P_2O_6$. Calculated %: P 18.78

4. Dipropyl 1-(Diethoxyphosphinyl)-1-methylpropyl Phosphite. Reaction was between 21 g of diethyl 1-hydroxy-1-methylpropylphosphonate, 10.1 g of triethylamine, and 18.45 g of dipropyl phosphorochloridite. The reaction was carried out under the conditions described above. The first distillation of the crude product yielded the fractions:

Fraction I, b.p. to 127° (1 mm); 7.5 g
Fraction II, b.p. 127-130° (1 mm); 22.2 g
Residue 3.5 g

Distillation of Fraction II yielded 16.7 g (46.65%) of a substance having b.p. 136.5-138° (1.5 mm); n_D^{20} 1.4435; d_4^{20} 1.0570; found MR 89.88; calculated for $C_{14}H_{32}P_2O_6$ MR 90.84.

Found %: P 17.58; 17.64

$C_{14}H_{32}P_2O_6$. Calculated %: P 17.32

5. Diisobutyl 1-(Diethoxyphosphinyl)ethyl Phosphite. Reaction was between 14 g of diethyl 1-hydroxyethylphosphonate, 16.5 g of diisobutyl phosphorochloridite, and 7.9 g of triethylamine. Fractional distillation of the product yielded the following fractions:

Fraction I, b.p. to 128° (1 mm); 4.5 g
Fraction II, b.p. 128-135° (1 mm); 20.4 g
Residue 3 g

Distillation of Fraction II yielded 14.6 g (52.25%) of a substance having b.p. 128-128.5° (1 mm); n_D^{20} 1.4372; d_4^{20} 1.0345; found MR 90.70; calculated for $C_{14}H_{32}P_2O_6$ MR 90.83.

Found %: P 17.76; 17.71

$C_{14}H_{32}P_2O_6$. Calculated %: P 17.31

6. Diisobutyl 1-(Diethoxyphosphinyl)-1-methylethyl Phosphite. Reaction was between 19.6 g of diethyl 1-hydroxy-1-methylethylphosphonate, 21.25 g of diisobutyl phosphorochloridite, and 10.1 g of triethylamine. Distillation of the product yielded the following fractions:

Fraction I, b.p. 75-130° (1.5 mm); 13.7 g
Fraction II, b.p. 130-135° (1.5 mm); 20.5 g
Residue 1.5 g

Distillation of Fraction II yielded 17.9 g (48.12%) of a substance having b.p. 126-127° (1 mm); n_D^{20} 1.4390; d_4^{20} 1.0277; found MR 95.21; calculated for $C_{15}H_{34}P_2O_6$ MR 95.46.

Found %: P 17.00; 17.02

$C_{15}H_{34}P_2O_6$. Calculated %: P 16.67

Action of Halogen Compounds on Dialkyl 1-(Diethoxyphosphinyl)alkyl Phosphites (Table 2)

1. Action of Ethyl Bromoacetate on Diethyl 1-(Diethylphosphinyl)ethyl Phosphite. Diethyl 1-(diethylphosphinyl)ethyl phosphite (6 g) was introduced into a round-bottomed flask fitted with condenser, thermometer, and dropping funnel. The ester was heated to 120°, and 3.1 g of ethyl bromoacetate was added. The temperature of the reaction mixture rose rapidly to 140°. The ethyl bromide that separated in the course of the reaction was collected in a receiver. The reaction flask was heated for one hour in a bath at 140-145°, and its contents were then distilled. The main fraction, amounting to 3.9 g (54.5%), had b.p. 170-171.5° (1 mm); n_D^{20} 1.4425; d_4^{20} 1.1761; found MR 81.07; calculated for $C_{12}H_{26}P_2O_6$ MR 81.15.

Found %: P 17.57; 17.51

$C_{12}H_{26}P_2O_6$. Calculated %: P 17.22

This substance is a colorless mobile liquid having only a feeble ethereal odor. It is readily soluble in water and organic solvents.

2. Action of Ethyl Bromoacetate on Diethyl 1-(Diethoxyphosphinyl)-1-methylethyl Phosphite. Reaction was between 7.3 g of diethyl 1-(diethoxyphosphinyl)-1-methylethyl phosphite and 3.9 g of ethyl bromoacetate. Evolution of ethyl bromide began at 130°. The temperature of the reaction mixture was raised to 145° and maintained at that level for 45 minutes. Distillation yielded a main fraction, amounting to 3.9 g (47.56%), having b.p. 169-170.5° (1 mm); n_D^{20} 1.4450; d_4^{20} 1.1570; found MR 86.03; calculated for $C_{13}H_{28}P_2O_6$ MR 85.62.

Found %: P 17.10; 17.15

$C_{13}H_{28}P_2O_6$. Calculated %: P 17.32

This substance is a colorless, almost odorless, mobile liquid. It is readily soluble in water and organic solvents.

3. Action of Ethyl Iodide on Diethyl 1-(Diethoxyphosphinyl)ethyl Phosphite. A mixture of 7.9 g of diethyl 1-(diethoxyphosphinyl)ethyl phosphite and 1 ml of ethyl iodide was sealed in a tube and heated for four hours at 135-140°. When the tube was cooled, it was observed that the volume of liquid had diminished somewhat. The contents were transferred to an Arbuzov flask and fractionated. The main fraction, amounting to 6.3 g (81.0%) had b.p. 141.5-143° (1 mm); n_D^{20} 1.4370; d_4^{20} 1.1295; found MR 70.05; calculated for $C_{10}H_{24}P_2O_6$ MR 70.11.

Found %: P 20.20

$C_{10}H_{24}P_2O_6$. Calculated %: P 20.53

4. Action of Ethyl Iodide on Diethyl 1-(Diethoxyphosphinyl)-1-methylethyl Phosphite. A mixture of 7.9 g of diethyl 1-(diethoxyphosphinyl)-1-methylethyl phosphite and 1 ml of ethyl iodide was heated in a sealed tube at 135-140° for four hours. Distillation of the isomerization product yielded 5.4 g (69.6%) of a main fraction having b.p. 140-141.5° (2 mm); n_D^{20} 1.4395; d_4^{20} 1.1165; found MR 74.52; calculated for $C_{11}H_{26}P_2O_6$ MR 74.73.

Found %: P 19.30; 19.25

$C_{11}H_{26}P_2O_6$. Calculated %: P 19.62

This substance is a colorless odorless mobile liquid. It is readily soluble in water and organic solvents.

5. Action of Propyl Bromide on Dipropyl 1-(Diethoxyphosphinyl)ethyl Phosphite. A mixture of 8 g of dipropyl 1-(diethoxyphosphinyl)ethyl phosphite and 1 ml of propyl bromide was heated in a sealed tube at 150-155° for six hours. Distillation from an Arbuzov flask yielded the following fractions:

Fraction I, b.p. 92-137° (1-2 mm); 1 g
Fraction II, b.p. 137-140° (1-0.5 mm); 1.5 g
Fraction III, b.p. 140-142° (0.5 mm); 3 g

Fraction III had n_D^{20} 1.4388; d_4^{20} 1.0879; found MR 79.75; calculated for $C_{12}H_{28}P_2O_6$ MR 79.49.

Found %: P 18.39; 18.29

$C_{12}H_{28}P_2O_6$. Calculated %: P 18.23

Addition of Sulfur to Dialkyl 1-(Diethoxyphosphinyl)alkyl Phosphites (Table 3)

1. Addition of Sulfur to Diethyl 1-(Diethoxyphosphinyl)ethyl Phosphite. A mixture of 10 g of diethyl 1-(diethoxyphosphinyl)ethyl phosphite, 1.06 g of sulfur powder, and 10 ml of benzene was prepared in a flask fitted with reflux condenser. The reaction mixture was heated for some time at the boiling point of benzene. The solvent was then removed, and the residue was vacuum-distilled. The main fraction, amounting to 6.9 g (62.72%), had b.p. 145-146° (1 mm); n_D^{20} 1.4561; d_4^{20} 1.1526; found MR 78.79; calculated for $C_{10}H_{24}P_2O_6S$ MR 78.74.

Found %: P 18.89; 18.85; S 9.48; 9.68

$C_{10}H_{24}P_2O_6S$. Calculated %: P 18.56; S 9.58

This substance is a colorless mobile liquid having a feeble sulfur-compound odor. It is readily soluble in organic solvents, but sparingly soluble in water.

2. Addition of Sulfur to Dipropyl 1-(Diethoxyphosphinyl)ethyl Phosphite. Reaction was between 10 g of the mixed phosphorous ester, 0.97 g of sulfur, and 10 ml of benzene. Distillation of the crude product yielded 8.3 g (75.66%) of a substance having b.p. 156-157° (1 mm); n_D^{20} 1.4550; d_4^{20} 1.1166; found MR 87.96; calculated for $C_{12}H_{28}P_2O_6S$ MR 88.12.

Found %: P 17.53; 17.52

$C_{12}H_{28}P_2O_6S$. Calculated %: P 17.13

This compound is a colorless mobile liquid having a sulfur-compound odor. It is very sparingly soluble in water, but readily soluble in organic solvents.

3. Addition of Sulfur to Diethyl 1-(Diethoxyphosphinyl)-1-methylethyl Phosphite. Sulfur (0.81 g) was sprinkled in small portions into a solution of 8 g of diethyl 1-(diethoxyphosphinyl)-1-methylethyl phosphite in 8 ml of benzene. The temperature rose by 8°. The reaction flask was heated in a glycerol bath at 50-90°. After some time the whole of the sulfur went into solution. The solvent was distilled off, and the reaction product was vacuum-distilled, when it yielded the fractions:

Fraction I, b.p. 105-138° (3-2 mm); 0.5 g
Fraction II, b.p. 138-145° (1.5 mm); 0.5 g
Fraction III, b.p. 145-146° (1.5 mm); 5 g

Fraction III, obtained in 56.7% yield, had n_D^{20} 1.4576; d_4^{20} 1.1419; found MR 83.1; calculated for $C_{11}H_{26}P_2O_6S$ MR 83.35.

Found %: P 17.86; 18.06

$C_{11}H_{26}P_2O_6S$. Calculated %: P 17.81

4. Addition of Sulfur to Dipropyl 1-(Diethoxyphosphinyl)-1-methylpropyl Phosphite. Sulfur (0.7 g) was added to a solution of 8 g of dipropyl 1-(diethoxyphosphinyl)-1-methylpropyl phosphite in 10 ml of benzene. The mixture was heated for a short time, the benzene was distilled off, and the residue was vacuum-fractionated. The following fractions were obtained.

Fraction I, b.p. 95-155° (2-1 mm); 1.4 g
Fraction II, b.p. 155-161° (1 mm); 0.5 g
Fraction III, b.p. 161-162° (1 mm); 3.2 g
Residue 1 g

The yield of Fraction III was 36.7%. It had n_D^{20} 1.4598; d_4^{20} 1.1017; found MR 96.92; calculated for $C_{14}H_{32}P_2O_6S$ MR 97.21.

Found %: P 15.82; 15.70; S 8.12; 8.10

$C_{14}H_{32}P_2O_6S$. Calculated %: P 15.89; S 8.2

This substance is a colorless mobile liquid having a sulfur-compound odor. It is soluble in water, and very readily soluble in alcohol, benzene, and other organic solvents.

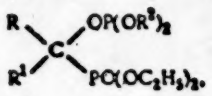
5. Addition of Sulfur to Diisobutyl 1-(Diethoxyphosphinyl)ethyl Phosphite. Reaction was between 10 g of diisobutyl 1-(diethoxyphosphinyl)ethyl phosphite and 0.86 g of sulfur; it was carried out in benzene solution. Distillation of the product yielded a main fraction, amounting to 7.1 g (65.26%); having b.p. 151-152.5° (1 mm); n_D^{20} 1.4525; d_4^{20} 1.0843; found MR 97.12; calculated for $C_{14}H_{32}P_2O_6S$ MR 97.21.

Found %: P 16.30; 16.21

$C_{14}H_{32}P_2O_6S$. Calculated %: P 15.89

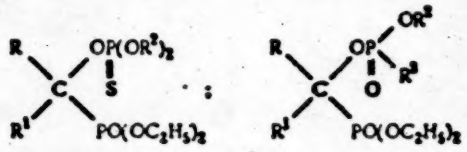
SUMMARY

1. By the action of dialkyl phosphorochloridites on 1-hydroxyalkylphosphonic esters in presence of triethylamine, some mixed phosphorous esters were obtained, namely, dialkyl 1-(diethoxyphosphinyl)alkyl phosphites of general formula:



in which R is H or alkyl, and R^1 and R^2 are alkyls.

2. From these substances, by the action of sulfur and by the action of halogen compounds, two series of substances having the following formulas were prepared:



and their physical constants were determined.

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[1] A. E. Arbuzov and P. I. Alimov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 5, 530.

[2] V. S. Abramov, J. Gen. Chem., 22, 4, 647 (1952)(T. p. 709)*.

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* T. p. = C. B. Translation pagination.

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ADDITION REACTIONS OF PERFLUOROOLEFINS

COMMUNICATION 4. REACTION OF VINYLIDENE FLUORIDE WITH SULFUR CHLORIDES AND WITH ALKANESULFENYL CHLORIDES

I. L. Knunyants and E. G. Vykhovskaya

In the preceding communication [1] the products of the addition of sulfur chlorides to tetrafluoroethylene were described. In the present paper we report the results of a study of the reaction of vinylidene fluoride with sulfur chlorides and with alkanesulfenyl chlorides.

The reaction between sulfur dichloride and vinylidene fluoride was carried out in a medium of dry carbon tetrachloride in a rotating steel autoclave. From the reaction mixture we succeeded in isolating bis(2-chloro-2,2-difluoroethyl) disulfide (I) in 15-20% yield. The fraction coming over before the disulfide contained several substances that were able to liberate iodine from acidified potassium iodide solution and to add vigorously to cyclohexene, but we did not succeed in isolating any individual substances from this fraction.

The reaction between vinylidene fluoride and sulfur monochloride proceeded in a more simple fashion. Thus, when the reactants were heated in a medium of dry carbon tetrachloride at 100° for 3-4 hours in a rotating steel autoclave (in presence of traces of hydroquinone), the same bis(2-chloro-2,2-difluoroethyl) disulfide (I) was isolated in 65-70% yield (calculated on the amount of vinylidene fluoride that reacted):

$$CF_2=CH_2 + S_2Cl_2 \longrightarrow \begin{matrix} S-CH_2CF_2Cl \\ | \\ S-CH_2CF_2Cl \end{matrix}$$

(I)

In addition to the disulfide, the reaction mixture contained a high-boiling residue – probably a mixture of polysulfides. By careful fractionation of the high-boiling products, some bis(2-chloro-2,2-difluoroethyl) trisulfide was isolated:

$$S_3(CH_2CF_2Cl)_2.$$

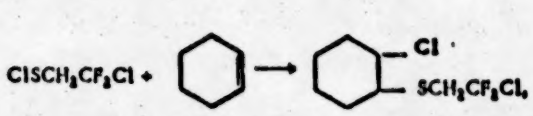
(II)

In order to prove the structure of bis(2-chloro-2,2-difluoroethyl) disulfide, it was treated with chlorine:

$$\begin{matrix} S-CH_2CF_2Cl \\ | \\ S-CH_2CF_2Cl \end{matrix} + Cl_2 \longrightarrow 2ClSCH_2CF_2Cl.$$

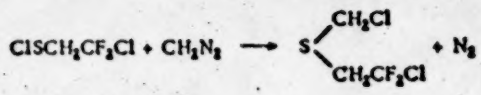
(III)

The 2-chloro-2,2-difluoroethanesulfenyl chloride (III) then formed was found to undergo many reactions characteristic of alkanesulfenyl chlorides. Thus, treatment with cyclohexene yielded 2-chlorocyclohexyl 2-chloro-2,2-difluoroethyl sulfide:



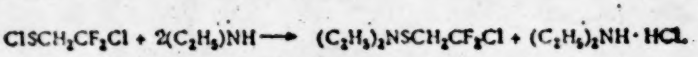
(IV)

and treatment with an ethereal solution of diazomethane yielded 2-chlorocyclohexyl chloromethyl sulfide:



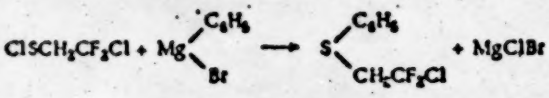
(V)

When an ethereal solution of the sulfenyl chloride was treated with diethylamine, the corresponding sulfenamide (VI) was readily formed:



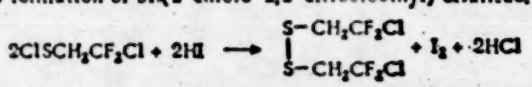
(VI)

Reaction of 2-chloro-2,2-difluoroethanesulfenyl chloride with phenylmagnesium bromide yielded 2-chloro-2,2-difluoroethyl phenyl sulfide:

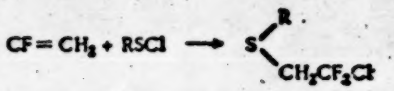


(VII)

Treatment of an ethereal solution of 2-chloro-2,2-difluoroethanesulfenyl chloride with aqueous potassium iodide resulted in the formation of bis(2-chloro-2,2-difluoroethyl) disulfide:

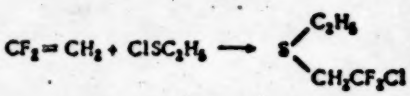


Apart from the addition reactions between vinylidene fluoride and sulfur chlorides, we carried out addition reactions between vinylidene fluoride and various alkanesulfenyl chlorides. The reaction was generally carried out by heating the reactants together in a medium of dry carbon tetrachloride in an autoclave; it resulted in the formation of the corresponding sulfides:



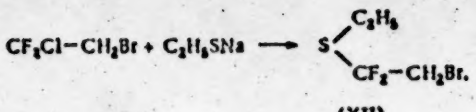
In this way we prepared 2-chloro-2,2-difluoroethyl ethyl sulfide (R = C_2H_5), 2-chloroethyl 2-chloro-2,2-difluoroethyl sulfide (R = CH_2CH_2Cl), 2-chloro-2,2-difluoroethyl 2-chloropropyl sulfide (R = $CH_2CHCl-CH_3$), and bis(2-chloro-2,2-difluoroethyl) sulfide (R = CH_2CF_2Cl); experiment showed that the last compound cannot be obtained by the direct reaction of vinylidene fluoride with sulfur chlorides.

In spite of the almost complete absence of doub. about the structures of the sulfides obtained — the mechanism of their formation and the direction of the addition being determined by the marked polarity of the starting substances — it was desirable to confirm their structures experimentally. It was thought that the reaction of 2-bromo-1-chloro-1,1-difluoroethane with thiols should result in the formation of the sulfide that was obtained also by reaction of vinylidene fluoride with ethanesulfenyl chloride:

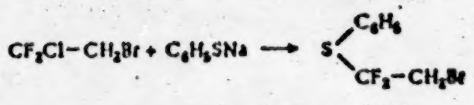


(VIII)

Experiment showed, however, that 2-bromo-1-chloro-1,1-difluoroethane reacts with benzene- and ethane-thiols with formation of 2-bromo-1,1-difluoroethyl ethyl sulfide and 2-bromo-1,1-difluoroethyl phenyl sulfide, respectively:



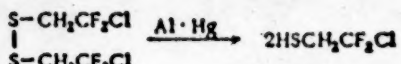
(XII)



(XIII)

The bromine atom of 2-bromo-1-chloro-1,1-difluoroethane is found to be very greatly stabilized by the neighboring chlorodifluoromethyl group. The stablization of bromine by proximity with a chlorodifluoromethyl group has been observed several times previously [2].

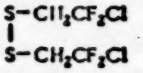
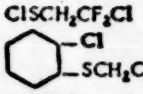
The direction of the addition of sulfur chlorides to vinylidene fluoride was proved conclusively by the formation of 2-chloro-2,2-difluoroethanethiol as the result of the reduction of bis(2-chloro-1,1-difluoroethyl) disulfide with amalgamated aluminum in a medium of moist ether:



(XIV)

2-Chloro-2,2-difluoroethanethiol was found to be quite stable; it is a colorless mobile liquid having the unpleasant odor that is characteristic of thiols. The formation of a stable compound could scarcely be expected if addition is in the opposite direction, since not a single compound is known in which two fluorine atoms and a hydroxyl or thiol group are to be found on the same carbon atom.

TABLE

Formula of compound	B.p. in °C (p in mm)	d_4^{20}	Refractive index n_D^{20}
	62 (3)	1.531	1.4500
$S_2(CH_2CF_2Cl)_2$	93-95 (7)	1.588	1.494
$ClSCH_2CF_2Cl$	110-112	1.523	1.448
	129-130 (9)	1.324	1.4870
$CH_2ClSCH_2CF_2Cl$	57-58 (25)	1.468	1.5550
$(C_2H_5)_2NSCH_2CF_2Cl$	52-54 (7)	1.169	1.4370
$C_6H_5SCH_2CF_2Cl$	103-104 (11)	1.313	1.5270
$C_2H_5SCH_2CF_2Cl$	35 (30)	1.205	1.4340
$CH_2ClCH_2SCH_2CF_2Cl$	55-56 (7)	1.4237	1.4650
$CH_3CHClCH_2SCH_2CF_2Cl$	93 (5)	1.390	1.4325
$CF_3ClCH_2SCH_2CF_2Cl$	78 (50)	1.526	1.4200
$C_2H_5SCF_2CH_2Br$	67-68 (32)	1.505	1.469
$C_6H_5SCF_2CH_2Br$	123 (14)	1.553	1.540
$HSCH_2CF_2Cl$	75-76	1.344	1.405

It was in fact found that no 2-chloro-2,2,1,1-tetrafluoroethanethiol could be obtained by the reduction of bis(2-chloro-2,2,1,1-tetrafluoroethyl) disulfide; in this reaction sulfur was precipitated and resinous products were formed.

The structures of our products are therefore beyond doubt. The constants of these compounds are given in the table.

EXPERIMENTAL

Bis(2-chloro-2,2-difluoroethyl) Disulfide. a) Dry carbon tetrachloride (30 ml) and sulfur dichloride (10 g) were introduced into a 100-ml rotating steel autoclave. The autoclave was then cooled, and 13 g of liquid vinylidene fluoride was introduced. The autoclave was set aside for one day at room temperature. The solvent was distilled off, and the residue was vacuum-distilled. A fraction of b.p. 63-65° (3 mm) was collected (20% yield). It was a clear colorless liquid of unpleasant odor, and had d_{20}^{20} 1.531; n_D^{20} 1.4500; found MR 46.01; calculated for $C_4H_4F_4Cl_2S$ MR 46.16.

Found %: Cl 26.90; F 29.66; S 24.10

$C_4H_4F_4Cl_2S$. Calculated %: Cl 26.99; F 28.90; S 24.30

b) A mixture of 12 g of sulfur monosulfide, 0.1 g of hydroquinone, and 15 ml of dry carbon tetrachloride was prepared in a 100 ml stainless steel autoclave. The autoclave was cooled, and 15 g of vinylidene fluoride was introduced. The autoclave was then heated at 90-100° for 4-6 hours with constant rotation. After removal of unchanged olefin and solvent by distillation, the residue was vacuum-fractionated:

Fraction I, b.p. 63-65° (3 mm); yield 15 g (65%)
Fraction II, b.p. 80-120° (4 mm); yield 3 g

Fraction I was bis(2-chloro-2,2-difluoroethyl) disulfide – a colorless very mobile liquid of unpleasant odor; d_{20}^{20} 1.533; n_D^{20} 1.4500.

Bis(2-chloro-2,2-difluoroethyl) Trisulfide. The residue remaining after the removal of the disulfide by distillation was repeatedly fractionated. A fraction boiling at 93-95° (7 mm) was collected; it was a clear yellowish liquid of unpleasant odor: d_{20}^{20} 1.588; n_D^{20} 1.494; found MR 54.07; calculated for $C_4H_4F_4Cl_2S_3$ MR 54.48.

Found %: Cl 23.78; F 24.70; S 32.05

$C_4H_4F_4Cl_2S_3$. Calculated %: Cl 24.07; F 25.76; S 32.54

2-Chloro-2,2-difluoroethanesulfenyl Chloride. Bis(2-chloro-2,2-difluoroethyl) disulfide (12 g) was introduced into a round-bottomed flask provided with a calcium chloride tube and a tube for the passage of gas. A stream of dry chlorine was passed in until the increase in weight was 3 g. Reaction was accompanied by the evolution of much heat. The solution acquired a deep orange color. The reaction mixture was fractionated through a column at atmospheric pressure. An 80% yield of 2-chloro-2,2-difluoroethanesulfenyl chloride, b.p. 110-112° was obtained. It is a bright-yellow, readily mobile liquid having a sharp odor typical of sulfenyl chlorides: d_{20}^{20} 1.523; n_D^{20} 1.448, found MR 29.35; calculated for $C_2H_2F_2Cl_2S$ MR 29.09.

Found %: active Cl 21.98; total Cl 42.35; F 22.66; S 19.61

$C_2H_2F_2Cl_2S$. Calculated %: active Cl 21.24; total Cl 42.51; F 22.75; S 19.16

Bis(2-chloro-2,2-difluoroethyl) Disulfide. A solution of 10 g of 2-chloro-2,2-difluoroethanesulfenyl chloride in ether was introduced into a separating funnel, and an excess of 10% aqueous potassium iodide was added in small portions. The ether solution was separated, washed with thiosulfate solution until colorless, and dried with sodium sulfate. The ether was distilled off, and the residue was distilled under reduced pressure. Two distillations yielded the pure disulfide in 85% yield. It had b.p. 62° (3 mm), d_{20}^{20} 1.53 and n_D^{20} 1.452.

2-Chlorocyclohexyl 2-Chloro-2,2-difluoroethyl Sulfide. 2-Chloro-2,2-difluoroethanesulfenyl chloride (6 g) was added slowly with shaking to excess of cyclohexene. The color of the sulfenyl chloride disappeared immediately, and much heat was evolved. The excess of cyclohexene was distilled off, and the residue was vacuum-distilled. After the second distillation the boiling point of the product was 129-130° (9 mm); it had d_{20}^{20} 1.324; n_D^{20} 1.487; found MR 54.13; calculated for $C_8H_{12}F_2Cl_2S$ MR 54.17.

Found %: Cl 28.28; F 15.13; S 13.22

$C_8H_{12}F_2Cl_2S$. Calculated %: Cl 28.50; F 15.26; S 12.85

2-Chloro-2,2-difluoroethyl Chloromethyl Sulfide. At –5°, an ethereal solution of 2-chloro-2,2-difluoroethanesulfenyl chloride was slowly added to an excess of ethereal diazomethane. The excess of diazomethane was distilled

off, and the residue was vacuum-distilled. The product, which was obtained in 50% yield, boiled at 57-59° (25 mm). It is a colorless pleasant-smelling liquid; d_{20}^{20} 1.468; n_D^{20} 1.555; found MR 33.45; calculated for $C_3H_4F_2Cl_2S$ MR 33.70.

Found %: Cl 33.86; F 22.09; S 17.90

$C_3H_4F_2Cl_2S$. Calculated %: Cl 39.22; F 21.00; S 17.68

2-Chloro-N,N-diethyl-2,2-difluoroethanesulfenamide. A mixture of 11.5 g of 2-chloro-2,2-difluoroethanesulfenyl chloride and 70 ml of dry ether was prepared in a round-bottomed flask fitted with dropping funnel and reflux condenser, and a solution of 10 g of diethylamine in 60 ml of dry ether was added slowly. The precipitated diethylamine hydrochloride was filtered off, ether was distilled off, and the residue was distilled at reduced pressure. The product, obtained in 65% yield after the second distillation, boiled at 52-54° (7 mm) and had d_{20}^{20} 1.169; n_D^{20} 1.437; found MR 45.61; calculated for $C_6H_{12}NF_2ClS$ MR 46.10.

Found %: Cl 17.88; F 18.89; S 16.10

$C_6H_{12}NF_2ClS$. Calculated %: Cl 17.45; F 18.64; S 15.72

2-Chloro-2,2-difluoroethyl Phenyl Sulfide. Magnesium (1.8 g) and iodine (one crystal) were introduced into a round-bottomed flask fitted with stirrer, dropping funnel, and reflux condenser. A solution of 11 g of bromobenzene in ether was added gradually from the dropping funnel. When the whole of the bromobenzene had been added, the reaction mixture was heated at 40° for 30 minutes. Then, with cooling and stirring, a solution of 9 g of 2-chloro-2,2-difluoroethanesulfenyl chloride in dry ether was added. The reaction mixture was poured into water, and the ether layer was separated and dried with magnesium sulfate. Ether was distilled off, and the residue was fractionated at reduced pressure. The second distillation gave a colorless mobile liquid having a sharp unpleasant odor. It was obtained in 45% yield and had b.p. 103-104° (11 mm), d_{20}^{20} 1.313; n_D^{20} 1.5270; found MR 48.33; calculated for $C_8H_7F_2ClS$ MR 47.90.

Found %: Cl 17.20; F 18.60; S 15.34

$C_8H_7F_2ClS$. Calculated %: Cl 17.00; F 18.20; S 15.96

2-Chloro-2,2-difluoroethyl Ethyl Sulfide. A mixture of 11 g of ethanesulfenyl chloride and 11 g of liquid vinylidene fluoride was prepared in rotating steel autoclave. The autoclave was heated at 65-70° for eight hours with constant rotation. Unchanged vinylidene fluoride was distilled off, and the residue was distilled under reduced pressure. The second distillation gave 2-chloro-2,2-difluoroethyl ethyl sulfide in 20% yield. It is a highly mobile colorless liquid, b.p. 35° (30 mm), d_{20}^{20} 1.216; n_D^{20} 1.4276; found MR 33.34; calculated for $C_4H_7F_2ClS$ MR 33.04.

Found %: Cl 21.72; F 23.00; S 20.34

$C_4H_7F_2ClS$. Calculated %: Cl 22.11; F 23.67; S 19.93

2-Chloroethyl 2-Chloro-2,2-difluoroethyl Sulfide. A mixture of 20 ml of dry carbon tetrachloride, 10 g of 2-chloroethanesulfenyl chloride, and 10 g of vinylidene fluoride was prepared in a steel autoclave. The autoclave was heated at 60° for ten hours. Unchanged olefin and solvent were distilled off, and the residue was vacuum-distilled. The second distillation gave a slightly yellowish, readily mobile liquid having a feeble unpleasant odor. It was obtained in 35% yield and had b.p. 55-56° (7 mm), d_{20}^{20} 1.4237; n_D^{20} 1.4650; found MR 37.86; calculated for $C_4H_6F_2ClS$ MR 37.87.

Found %: Cl 36.71; F 19.55; S 16.36

$C_4H_6F_2Cl_2S$. Calculated %: Cl 36.41; F 19.48; S 16.41

2-Chloro-2,2-difluoroethyl 2-Chloropropyl Sulfide. A mixture of 20 ml of dry carbon tetrachloride, 13 g of 2-chloropropanesulfenyl chloride, and 10 g of vinylidene fluoride was prepared in an autoclave. The autoclave was heated at 100° for nine hours. Unchanged olefin and solvent were distilled off, and the residue was vacuum-distilled. The third distillation gave a substance boiling at 93° (5 mm) in 15% yield; a colorless readily mobile liquid having a feeble unpleasant odor; d_{20}^{20} 1.3903; n_D^{20} 1.4825; found MR 42.89; calculated for $C_5H_8F_2Cl_2S$ MR 42.50.

Found %: Cl 33.76; F 17.80; S 17.22

$C_5H_8F_2Cl_2S$. Calculated %: Cl 33.97; F 18.18; S 16.64

Bis(2-chloro-2,2-difluoroethyl) Sulfide. A mixture of 20 ml of dry carbon tetrachloride, 13 g of 2-chloro-2,2-difluoroethanesulfenyl chloride, and 10 g of vinylidene fluoride was prepared in a stainless steel autoclave. The

autoclave was heated at 90-95° for five hours. After removal of unchanged vinylidene fluoride and solvent by distillation, the residue was vacuum-distilled. The third distillation gave a product boiling at 78° (50 mm) in 50% yield. It was a very mobile colorless liquid having a very unpleasant odor; it had d_{20}^{20} 1.526; n_D^{20} 1.4200; found MR 37.69; calculated for $C_4H_4F_4Cl_2S$ MR 38.30.

Found %: Cl 30.81; F 32.25; S 14.42

$C_4H_4F_4Cl_2S$. Calculated %: Cl 30.74; F 32.90; S 13.85

A weighed amount of bis(2-chloro-2,2-difluoroethyl) sulfide and some alcoholic potash were introduced into a round-bottomed flask fitted with a reflux condenser. The mixture was heated for 40 minutes in a boiling water bath, and was then titrated for chloride by the Volhard method:

Found %: Cl 30.90

Calculated %: Cl 30.74

2-Bromo-1,1-difluoroethyl Ethyl Sulfide. A mixture of 30 ml of absolute methanol, 1.5 g of sodium, and 4 g of ethanethiol was prepared in flask fitted with reflux condenser and dropping funnel. 2-Bromo-1-chloro-1,1-difluoroethane (12 g) was then added slowly. The reaction mixture was heated for two hours in a water bath. The precipitated sodium chloride was then filtered off, and the residue was distilled under reduced pressure. After a second distillation the boiling point of the product was 67-68° (32 mm); it had d_{20}^{20} 1.505; n_D^{20} 1.469.

Found %: Br 39.10; F 18.07; S 15.83

$C_4H_7F_2BrS$. Calculated %: Br 39.02; F 17.07; S 15.61

2-Bromo-1,1-difluoroethyl Phenyl Sulfide. A mixture of 30 ml of absolute alcohol, 2.5 g of sodium, and 12 g of benzenethiol was prepared in a flask fitted with reflux condenser and dropping funnel. 2-Bromo-1-chloro-1,1-difluoroethane (20 g) was then added slowly. The reaction mixture was heated for one hour in a water bath, and was then poured into water. The precipitated oil was separated, washed with sodium bicarbonate solution and then water, dried, and distilled. The product was a pleasant-smelling colorless liquid boiling at 123° (14 mm) after the second distillation; it had d_{20}^{20} 1.553; n_D^{20} 1.540; found MR 51.10; calculated for $C_8H_7F_2BrS$ MR 50.90.

Found %: S 12.43; F 14.69; Br 32.02

$C_8H_7F_2BrS$. Calculated %: S 12.64; F 15.02; Br 31.65

2-Chloro-2,2-difluoroethanethiol. Bis(2-chloro-2,2-difluoroethyl) disulfide (6 g) was added to a suspension of amalgamated aluminum turnings in moist ether. Vigorous reaction was observed. The flask was allowed to stand at room temperature for two hours. Aluminum hydroxide was then filtered off, and the reaction mixture was distilled through an efficient column. The products were 2 g of a substance boiling at 75-76° and 3 g of unchanged disulfide [b.p. 62-64° (4 mm); d_{20}^{20} 1.530]. The substance of b.p. 75-76° was a very mobile colorless liquid having a sharp unpleasant odor typical of thiols. It gave a positive test for the thiol group. The yield, calculated on the amount of disulfide that reacted, was 70%. The substance had d_{20}^{20} 1.344; n_D^{20} 1.405; found MR 24.16; calculated for $C_2H_3F_2ClS$ MR 24.03.

Found %: Cl 27.20; F 28.55; S 24.10

$C_2H_3F_2ClS$. Calculated %: Cl 26.79; F 28.68; S 24.15

SUMMARY

1. By the addition of sulfur chlorides and of alkanesulfenyl chlorides to vinylidene fluoride, some new sulfenyl chlorides, sulfides, and polysulfides containing the 2-chloro-2,2-difluoroethyl group were obtained.

2. 2-Chloro-2,2-difluoroethanethiol was prepared by the reduction of bis(2-chloro-2,2-difluoroethyl) disulfide. 2-Bromo-1,1-difluoroethyl alkyl sulfides were prepared by the reaction of 2-bromo-1-chloro-1,1-difluoroethane with thiols.

Received May 20, 1954

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[1] I. L. Knunyants and A. V. Fokin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, No. 4, 705 (T.p. 627)*.

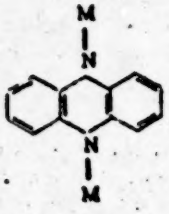
[2] E. T. McBee, Ind. Eng. Chem., 39, 236, (1947).

* T. p. = C. B. Translation pagination.

COMPLEX NATURE OF DIMETAL COMPOUNDS OF PHENAZINE

B. M. Mikhailov and A. N. Blokhina

We have established previously that phenazine readily forms compounds with alkali metals when 1,2-dimethoxyethane is used as solvent [1]. In presence of this solvent we succeeded in effecting the direct addition of sodium to phenazine, and we obtained the dilithium compound of phenazine by the metallization of 5,10-dihydrophenazine with phenyllithium. At that time the products were not isolated in the individual state and were not analyzed; their structure, as products of the addition of two metal atoms at the nitrogen atoms – i.e. as

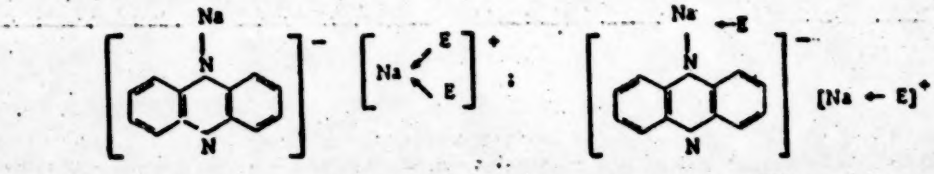


(I)

in which M is an alkali-metal atom – was assumed on the basis of their chemical reactions with various reagents (alkyl halides, ethylene oxide, etc.). In view of recent results relating to the complex nature of dimetal derivatives of unsaturated systems [2], the question arose of the investigation of the composition and structure of the dimetal compounds of phenazine.

The disodium compound was prepared for analysis by metallization of 5,10-dihydrophenazine with aid of 9,10-disodio-9,10-dihydroanthracene in 1,2-dimethoxyethane. This method is to be preferred to the direct addition of sodium to phenazine [1] in that it ensures the absence of admixture of fine particles of metal to the metal compound of phenazine. The dilithium compound was prepared in the same medium by the metallization of 5,10-dihydrophenazine with phenyllithium. Analysis of the dimetal compounds of phenazine for their contents of metal and phenazine showed that coordinated 1,2-dimethoxyethane was present – two molecules in the sodium compound, and six molecules in the lithium compound.

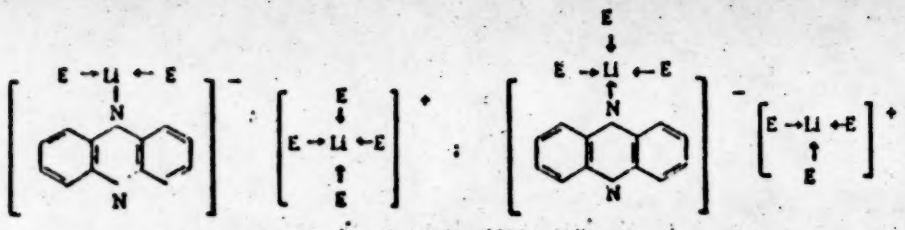
It follows from the fact that in 1,2-dimethoxyethane the dimetal compounds of phenazine conduct electricity that these compounds are ionized. On analogy with the dimetal compounds of anthracene and other unsaturated systems [2] it must be supposed that only one of the metal atoms is in the ionized state, whereas the other is attached to the heterocycle by a covalency. The structure of the disodium compound can then be represented by formula (II) or (III):



(II) (III)

In which E = $CH_3OCH_2-CH_2-OCH_3$.

For the structure of the dilithium compound two variants (IV) and (V) are again possible, the difference lying in the disposition of the diether molecules:



(IV) (V)

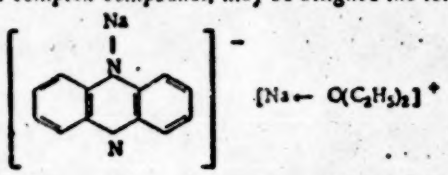
in which E = $CH_3OCH_2CH_2OCH_3$.

Since the metal ion has the greater tendency to undergo coordination, the more probable structure for the dilithium compound of phenazine is (IV), in which the metal ion is coordinately saturated.

In connection with the establishment of the complex nature of the dimetal compounds of phenazine prepared in a 1,2-dimethoxyethane medium, it was of interest to re-examine Schlenk and Bergmann's results [3] on the composition of the sodium compound of phenazine which they obtained in an ether medium by the action of the disodium derivative of N-(diphenylmethylene)aniline on phenazine. They assumed, solely on the basis of the determination of the metal content (11.3%) that the product was the molecular compound formed by 9,10-disodio-9,10-dihydrophenazine with a molecule of phenazine.

The authors did not describe their experiments, although it was essential to do so. On repeating their work, we found that, when only a slight excess of the disodium derivative of N-(diphenylmethylene)aniline is used, the metal contents of the products vary greatly from one experiment to another; reproducible results are obtained only when a large excess of this reagent is used. Under these conditions, a substance containing 15.6-16% of sodium and 61-62% of phenazine is obtained, whereas, for a molecular compound of disodiodihydrophenazine with phenazine such as Schlenk and Bergmann thought they had obtained, the sodium content should be 11.33% and the phenazine content 88.67%.

The metal and phenazine contents of our phenazine disodium compound correspond to a monoetherate, which, by analogy with the above-described complex compounds, may be assigned the following structure (VI):



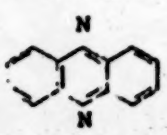
(VI)

EXPERIMENTAL

All operations were carried out in an atmosphere of nitrogen. The metal compounds of phenazine were prepared in two-legged tubes.

Complex Compound formed by 5,10-Dilithio-5,10-dihydrophenazine with 1,2-Dimethoxyethane

5,10-Dihydrophenazine (0.6 g) was dissolved in 9 ml of 1,2-dimethoxyethane, and to the resulting solution 30 ml of an ethereal solution of two equivalents of phenyllithium was added. The brown precipitate that separated was filtered off through a special filter funnel [4], washed with 1,2-dimethoxyethane, and dried to constant weight in a vacuum. The complex was then covered with a layer of ether, and an ethereal solution of methanol was added. Water was then added, and the metal content of the aqueous layer was determined. Solvent was distilled from the ethereal layer, and the residue was dried to constant weight in a vacuum desiccator. The difference between the weight of the complex and the sum of the weights of phenazine (obtained in the form of 5,10-dihydrophenazine) and lithium was equal to the weight of the coordinately bound 1,2-dimethoxyethane.



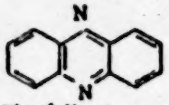
$\cdot 2Li \cdot 6C_4H_{10}O_2$. Found %: Li 2.08; 2.06; phenazine 24.83; 25.11

Calculated %: Li 1.89; phenazine 24.62

The following results were obtained for the conductance of the dilithium compound of phenazine in 1,2-dimethoxyethane: molar volume $g = 565$ liters, specific conductance $\kappa = 4.47 \cdot 10^{-6}$ $cm^{-1} \cdot ohm^{-1}$, molar conductance $\lambda = 0.252$ $cm^{-1}ohm^{-1}$.

Complex Compound formed by 5,10-Disodium-5,10-dihydrophenazine with 1,2-dimethoxyethane

A solution of 0.7 g of dihydrophenazine in 10 ml of 1,2-dimethoxyethane was added to a filtered solution of the disodium compound of anthracene prepared by shaking a mixture of 1 g of anthracene, 0.3 g of sodium, and 15 ml of 1,2-dimethoxyethane for 25 hours. The brick-red precipitate was filtered off, washed with 1,2-dimethoxyethane, dried to constant weight, and analyzed as described above.



$2Na \cdot 2C_4H_{10}O_2$.

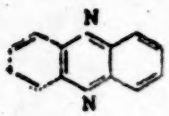
Found %: Na 10.90; 11.05; phenazine 46.25; 45.00

Calculated %: Na 11.32; phenazine 44.34

The following results were obtained for the conductance of the disodium compound of phenazine in 1,2-dimethoxyethane: molar volume $g = 160$ liters, specific conductance $\kappa = 5.16 \cdot 10^{-6}$ $cm^{-1}ohm^{-1}$, molar conductance $\lambda = 0.825$ $cm^{-1}ohm^{-1}$.

Complex Compound formed by 5,10-Disodio-5,10-dihydrophenazine with Diethyl ether

A mixture of 4.5 g of N-(diphenylmethylene)aniline, 1.1 g of sodium, and 80 ml of ether was shaken for 50 hours. The cherry-red solution of the disodium derivative of N-(diphenylmethylene) aniline was filtered, and a solution of 0.6 g of phenazine in 50 ml of ether was added. The resulting precipitate was filtered off, washed with ether, dried to constant weight, and analyzed as described above.



$2Na \cdot (C_2H_5)_2O$.

Found %: 16.0; 15.9; phenazine 62.20; 61.30

Calculated %: Na 15.3; phenazine 60.0

SUMMARY

1. Dimetal compounds of phenazine prepared in a medium of 1,2-dimethoxyethane are complex compounds. The disodium compound contains two molecules of 1,2-dimethoxyethane, and the dilithium compound contains six molecules of 1,2-dimethoxyethane.

2. In 1,2-dimethoxyethane solution, dimetal compounds of phenazine conduct electricity and have an ionic structure. In these compounds, one alkali-metal atom forms part of a complex cation, and the other is covalently bound to the negatively charged phenazine molecule.

3. The disodium compound of phenazine prepared in ether by the action of the disodium derivative of N-(diphenylmethylene)aniline on phenazine is a complex compound, each molecule of which contains one molecule of ether.

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CATALYTIC HYDROGENATION OF DOUBLY UNSATURATED COMPOUNDS HAVING A CONJUGATED SYSTEM OF DOUBLE BONDS

COMMUNICATION 3. HYDROGENATION OF 2,3-DIMETHYL-1,3-BUTADIENE IN PRESENCE OF PLATINUM, NICKEL, AND PALLADIUM

I. V. Gostunskaya, G. V. Loza, and B. A. Kazansky

The present work forms a continuation of our investigations into the laws governing the addition of a catalytically activated hydrocarbon to a conjugated diene hydrocarbon in presence of platinum, palladium, and nickel. A paper by Kazansky and Popova [1] describes the reduction of bisocrotyl (2,5-dimethyl-2,4-hexadiene) – a hydrocarbon in which methyl groups are attached to the first and fourth carbon atoms of the conjugated system. Hydrogen added mainly at the 1,2-positions of the conjugated system. The content of 2,5-dimethyl-3-hexene – the hydrocarbon formed by 1,4-addition – was 13%, 6%, or 9% for hydrogen over platinum, palladium, or nickel, respectively.

In the hydrogenation of isoprene [2] – a diene hydrocarbon in which there is a methyl group on the second atom of the conjugated system – the character of the addition of hydrogen, while not greatly different in the case of platinum, is greatly changed in the case of nickel and palladium: the contents of 2-methyl-2-butene – the product of 1,4-addition of hydrogen – are 15% for platinum, 41% for palladium, and 40% for nickel.

The present work was undertaken with the object of elucidating the effect of two methyl groups on the second and third atoms of the conjugated system, the hydrocarbon examined being 2,3-dimethyl-1,3-butadiene. The catalytic hydrogenation of this hydrocarbon has been studied by Lebedev [3] and by Dupont [4]. According to Lebedev's results, when one molecule of hydrogen adds to 2,3-dimethyl-1,3-butadiene in presence of platinum, a mixture of hydrocarbons of the following composition is obtained:

2,3-Dimethyl-1-butene	— 32 mole %
2,3-Dimethyl-2-butene	— 12 mole %
2,3-Dimethylbutane	— 28 mole %
2,3-Dimethyl-1,3-butadiene	— 28 mole %

The authors did not isolate individual hydrocarbons from the hydrogenation product, but derived their information from kinetic hydrogenation curves obtained after removal of unchanged diene.

Dupont studied the hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of Raney nickel, and he analyzed the hydrogenation products by the Raman spectrum method. The contents of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene in the hydrogenation products were 63% and 37%, respectively.

In the present work we have investigated the catalytic hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of platinum black, of palladium black, and of Raney nickel. The composition of the hydrogenation products was determined by the method employed in the previous investigations on bisocrotyl and isoprene, namely, by rectification of the reaction mixture through highly efficient columns and investigation of the composition of the fractions obtained (by determinations of refractive index, density, and bromine numbers). The use of the same method of investigation for different dienes in presence of different catalysts makes the results comparable and makes it possible to establish the effect of the structures of the original dienes and of the identity of the catalyst on the direction of addition of hydrogen.

Our study of the hydrogenation of 2,3-dimethyl-1,3-butadiene shows that, as in the case of the hydrogenation of isoprene and bisocrotyl, addition proceeds in all possible directions. The content of 2,3-dimethyl-2-butene – 1,3-addition product – in the reaction mixture is 13 mole % for hydrogenation over platinum and 25 mole % for

hydrogenation over nickel. In hydrogenation over platinum — as in all such cases studied by Lebedev and by us — addition of one molecular proportion of hydrogen results in the formation not only of monoolefins, but also of the fully hydrogenated product, some of the diene, therefore, remaining unchanged.

Comparison of the results for 2,3-dimethyl-1,3-butadiene and isoprene shows that the difference in the compositions of the reaction mixtures is inappreciable when platinum is used as catalyst, but the change is much greater when nickel is used, the proportion of 1,4-addition product being lower in the dimethylbutadiene hydrogenation products than in the isoprene hydrogenation products.

EXPERIMENTAL

Synthesis and Properties of 2,3-Dimethyl-1,3-butadiene. 2,3-Dimethyl-1,3-butadiene was prepared by the dehydration of pinacol, which was synthesized by Adams' method, as modified by Getling and Zhdanova [5]. The dehydration of pinacol was carried out by Lebedev's method [3], in which it is treated with phosphoric acid in acetic anhydride; this method gives a higher yield of the diene than any other method reported. The synthesized diene had the following constants: b.p. 69° (742 mm); n_D^{20} 1.4393; d_4^{20} 0.7266; found MR_D 29.70, calculated MR_D for $C_6H_{10}(F_2)$ 28.97. The literature [6] gives b.p. 68.9° (760 mm); n_D^{20} 1.4390; d_4^{20} 0.7263.

Hydrogenation Procedure and Investigation of the Hydrogenation Products. The hydrogenation of 2,3-dimethyl-1,3-butadiene was carried out at room temperature and under atmospheric pressure in a hydrogenation flask, which was shaken at the rate of 300 double shakes per minute. The amount of hydrogen adsorbed was measured in a 180 ml gas buret having 0.2ml graduations. Readings for the plotting of the hydrogenation curve were taken every 30 seconds. The platinum and palladium blacks were prepared by Wilstätter's method [7], and Raney nickel was prepared by Adkins' method [8]. The solvent used was 96% ethanol.

In the experiments on the composition of the products of the addition of one molecular proportion of hydrogen to the diene, reaction was allowed to proceed until the volume of hydrogen calculated for the given weight of diene had been absorbed. Distillation through a column yielded an azeotropic mixture of the hydrogenation products and alcohol, from which the alcohol was removed by washes with saturated calcium chloride solution. The hydrocarbon mixture was then distilled over sodium. In order to remove the unchanged diene present when the hydrogenation was carried out over platinum, the mixture of hydrocarbons was refluxed with maleic anhydride for one hour. The hydrocarbons obtained were identified by determining the boiling points, densities, refractive indices, and bromine numbers of the fractions [9]. The calculation of the amounts of the various hydrocarbons formed in the hydrogenation process was carried out on the basis of data from the fractionation curves and of the properties of the fractions.

Hydrogenation of 2,3-Dimethyl-1,3-butadiene in Presence of Platinum Black. In Table 1, we give the conditions under which two experiments on the hydrogenation of 2,3-dimethyl-1,3-butadiene were carried out with the object of determining the hydrogenation curves.

TABLE 1

Expt. No.	Amount of hydrocarbon (g)	Amount of catalyst (g)	Amount of alcohol (ml)	Temperature (°C at 740 mm)	Amount of hydrogen (ml)	
					absorbed	calculated
1	0.4083	0.0972	10.0	22	220	242
2	0.4097	0.0978	10.0	22	256	249

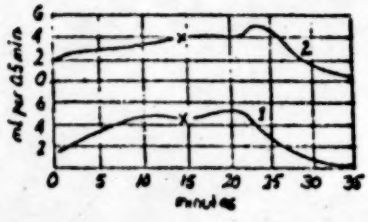

Fig. 1. Curve for the hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of platinum black: 1) Experiment 1; 2) Experiment 2.

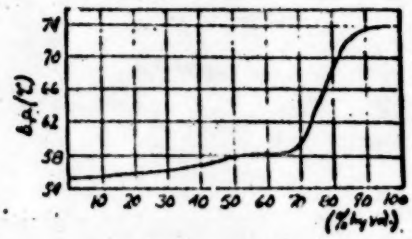

Fig. 2. Fractionation curve of the products of the addition of one molecular proportion of hydrogen to 2,3-dimethyl-1,3-butadiene in presence of platinum black.

The hydrogenation curve, which is given in Fig. 1, shows that in presence of platinum the hydrogenation process is complicated. The addition of one molecular proportion of hydrogen (the point at which this occurs is indicated on the curve by the sign ×) is not associated with any feature of the curve; a change in the rate of hydrogenation occurs when about 70% of the calculated amount of hydrogen has added. Our hydrogenation curves are very similar to those obtained by Lebedev.

Fig. 3. Curve for the hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of Raney nickel: 1) Experiment 1; 2) Experiment 2.

Fig. 5. Curve for the hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of palladium black.

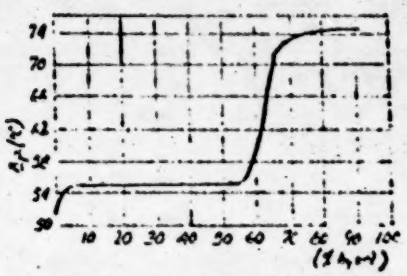

Fig. 4. Fractionation curve of the products of the addition of one molecular proportion of hydrogen to 2,3-dimethyl-1,3-butadiene in presence of Raney nickel.

With the object of studying the hydrogenation of 2,3-dimethyl-1,3-butadiene in greater detail, we carried out the 50% hydrogenation of 54.0 g of diene, i.e. the addition of one mole of hydrogen to one mole of diene. From the mixture with alcohol, 47.0 g of hydrogenation product was isolated, and the treatment of this with maleic anhydride yielded 32 g of a hydrocarbon mixture, which was then distilled through a 70-plate column. The results of the fractionation and the characteristics of the fractions obtained are given in Table 2; the fractionation curve is given in Fig. 2.

TABLE 2

Fraction No.	B.p. (°C at 760 mm)	Amount of fraction (% by weight)	n_D^{20}	d_4^{20}	MR Calculated	MR Found	Bromine number	Amount of olefins (%)	Amount of paraffin (%)
I	55.3-56.1	36.2	1.3882	0.6771	29.44 for C_6H_{12}	29.29	186.1	97.6	2.4
II	56.1-57.8	18.2	1.3822	0.6707	–	–	115.0	60.3	39.7
III	57.8-58.3	15.6	1.3741	0.6621	29.90 for C_6H_{14}	29.67	5.0	2.6	97.4
IV	58.3-72.2	10.9	1.4030	0.6940	–	–	96.2	50.5	49.5
V	72.2-73.5	7.5	1.4162	0.7112	29.44 for C_6H_{12}	29.39	•	–	–
Residue in still		3.8							
Total		92.2%							
Losses		7.8%							

• Agreeing results could not be obtained in the determination of the bromine number of Fraction V, which consisted mainly of 2,3-dimethyl-2-butene.

The constants of the hydrocarbons that could be formed by the hydrogenation of 2,3-dimethyl-1,3-butadiene are given in Table 3.

A comparison of the characteristics of the fractions with the data in Table 3 shows that Fraction I contains mainly 2,3-dimethyl-1-butene, Fraction III mainly 2,3-dimethylbutane, and Fraction V mainly 2,3-dimethyl-2-butene, probably with some unremoved diene as impurity, which raises the constants of Fraction V somewhat, as compared with those of the pure monoolefin. Fractions II and IV are intermediate fractions containing the saturated hydrocarbon in admixture with monoolefins, i.e. with 2,3-dimethyl-1-butene (Fraction II) and with 2,3-dimethyl-2-butene (Fraction IV). The compositions of the mixtures were determined with the aid of their bromine numbers. On the basis of the data in Table 2, the total contents of the various hydrocarbons in the mixture taken for fractionation (after removal of unchanged diene) were calculated. The calculation of the composition of the reaction mixture before removal of diene was based on Lebedev's rule, which states that the number of moles of diene and of saturated hydrocarbon are equal at the point at which one molecular proportion of hydrogen has added to the diene. The results of such calculations are given in Table 4.

TABLE 3

Hydrocarbon	B.p. (°C at 760 mm)	n_D^{20}	d_4^{20}	Literature reference
2,3-Dimethyl-1-butene	55.64	1.3904	0.6779	[10]
2,3-Dimethyl-2-butene	73.21	1.4122	0.7080	[10]
2,3-Dimethylbutane	57.99	1.3750	0.6616	[10]

TABLE 4

Hydrocarbon	Amount	
	After removal of diene (mole %)	Before removal of diene (mole %)
2,3-Dimethyl-1-butene	51.5	39
2,3-Dimethyl-2-butene	17.1	13
2,3-Dimethylbutane	31.4	24
2,3-Dimethyl-1,3-butadiene	—	24

TABLE 5

Expt. No.	Amount of hydrocarbon (g)	Amount of catalyst (g)	Amount of alcohol (ml)	Temperature (°C at 754 mm)	Amount of hydrogen (ml)	
					absorbed	calculated
1	0.3229	0.1151	25.0	18	108.0•	194
2	0.3344	0.1197	25.0	18	101.4•	199

• In view of the fact that, in its last stage, hydrogenation went with a very low, though constant velocity, the reaction was not carried out to completion.

TABLE 6

Fraction No.	B.p. (°C at 760 mm)	Amount of fraction (% by weight)	n_D^{20}	d_4^{20}	MR		Bromine number	Amount of olefins (%)
					Calculated	Found		
I	50-55.5	2.4	1.3879	—	for C_6H_{12}			
II	55.5	57.1	1.3903	0.6776	29.44	29.38	190	100
III	55.6-70.4	6.2	1.4250	0.7200	—	—	—	—
IV	70.5-73.9	16.5	1.4173	0.7185	—	—	—	—
V	73.9	10.2	1.4120	0.7114	29.44	29.38	•	—
Residue in still and losses		7.6						

• It was not found possible to determine the bromine number.

The predominating direction of the hydrogenation of 2,3-dimethyl-1,3-butadiene in presence of platinum black is addition of hydrogen at the 1,2-positions of the conjugated system. Our results are close to those of Lebedev.

Hydrogenation of 2,3-Dimethyl-1,3-butadiene in Presence of Raney Nickel. In Table 5 we give the conditions under which two experiments on the hydrogenation of 2,3-dimethyl-1,3-butadiene were carried out with the object of determining the hydrogenation curves. The hydrogenation curves are given in Fig. 3.

The hydrogenation curves for a nickel catalyst are greatly different from those for the platinum catalyst. The marked breaks in the curves occur at the points corresponding to the addition of one molecular proportion of hydrogen.

In order to study the products of reaction in presence of Raney nickel, the 50% hydrogenation of 51 g of 2,3-dimethyl-1,3-butadiene was carried out. From the mixture with alcohol, 44 g of hydrogenation products was isolated and were distilled in presence of hexane through a 70-plate column. The fractionation curves are given in Fig. 4. The results of the fractionation and the characteristics of the fractions obtained are given in Table 6.

Fractions I and II contain mainly 2,3-dimethyl-1-butene, Fraction III contains a mixture of 2,3-dimethyl-1-butene and unchanged diene, Fraction IV 2,3-dimethyl-2-butene with a little diene impurity, and Fraction V 2,3-dimethyl-2-butene. No completely hydrogenated product was found. On the basis of the fractionation curve and the data of Table 6, an approximate calculation was made of the composition of the mixture of hydrocarbons obtained in the hydrogenation:

2,3-Dimethyl-1-butene	—	26.8 g (66.6 mole %)
2,3-Dimethyl-2-butene	—	10.4 g (25.1 mole %)
2,3-Dimethyl-1,3-butadiene	—	3.4 g (8.3 mole %)

As in hydrogenation over platinum, in presence of nickel the main direction of the reaction is addition of hydrogen at the 1,2-positions of the conjugated system.

Hydrogenation of 2,3-Dimethyl-1,3-butadiene in Presence of Palladium Black. One experiment was carried out for the purpose of determining the kinetic curve. The amounts taken were 0.4950 g (0.006 mole) of diene and 0.0635 g (0.0006 mole) of catalyst. The diene was dissolved in 10 ml of ethanol. The hydrogenation was carried out at 21° and 750 mm. The amount of hydrogen absorbed in the hydrogenation of the diene was 261 ml, the amount required theoretically being 293 ml. The hydrogenation curve, which is given in Fig. 5, is close to that for the nickel catalyst. Unfortunately, we were unable to carry out the 50% hydrogenation of larger amounts of 2,3-dimethyl-1,3-butadiene in presence of palladium black.

SUMMARY

1. In presence of platinum or nickel, the hydrogenation of 2,3-dimethyl-1,3-butadiene proceeds in all possible directions.

2. Comparison of the results for the hydrogenation of 2,3-dimethyl-1,3-butadiene and of isoprene shows that, in presence of platinum, the relative extents of the addition of hydrogen in the various directions are approximately the same for both dienes, whereas in presence of nickel they are different.

3. In the hydrogenation of 2,3-dimethyl-1,3-butadiene in the presence of nickel, the amount of 1,4-addition product (25%) is less than in the hydrogenation of isoprene under similar conditions (40%).

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CATALYTIC DEHYDROCYCLIZATION OF PIPERYLENE

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There have been only a few isolated investigations on the contact-catalysis reactions of piperylene. Thus, Frank, Emmick, and Johnson [1] studied the thermal interconversion of the cis-and trans-isomers of piperylene at 600° and also the iodine-catalyzed interconversion of the isomers at the boiling point of the diene. They found that each of the pure piperylene isomers yields a mixture of cis- and trans-forms. At 600°, this mixture contains 40-45% of cis-piperylene, and at the boiling point in presence of iodine the equilibrium mixture, obtained after an 18-hour treatment, contains 87% of the trans-form.

Kennedy and Hetzel [2] investigated the catalytic reactions of piperylene in presence of $Al_2O_3 + Cr_2O_3$ and of aluminisilicates of various compositions. They observed that, in a vacuum at 600-620°, piperylene undergoes partial cracking with simultaneous formation of cyclopentadiene in a yield that, in some experiments, amounted to as much as 9% of the condensate. These authors consider that the cyclization reaction of piperylene is noncatalytic. It appeared to us that this conclusion was not sufficiently well grounded, and we therefore decided to make a more detailed study of the reaction. We have therefore investigated the reactions of piperylene at various temperatures and pressures in presence of various catalysts, and we have tried to determine the effect of the relative amounts of cis and trans isomers in the original piperylene on the yield of cyclopentadiene. At the same time we have observed the interconversion of cis- and trans-piperylenes under the action of the catalyst. From thermodynamic data for piperylene, as given by Kilpatrick, Beckett, Prosen, Pitzer, and Rossini [3], with the help of the approximate equation

$$-RT \ln K_p = \Delta H^\circ_{298.16^\circ} - T\Delta S^\circ_{298.16^\circ} = \Delta Z,$$

we calculated, on the one hand, the equilibrium constant for the interconversion of cis- and trans-piperylenes at their boiling points, and on the other hand, the logarithms of the cyclization-reaction constants for various temperatures. As no values of the thermodynamic potential were available for cyclopentadiene, we calculated these quantities from the corresponding quantities for cyclopentane and cyclopentene [4], neglecting the effect of the conjugation of the double bonds in cyclopentadiene and assuming that

$$\Delta Z_{\square} = 2\Delta Z_{\square} - \Delta Z_{\square}.$$

For the interconversion of the geometric isomers of piperylene we took ΔZ to be 35,816 and 36,025 cal/mole for the cis- and trans-forms respectively, and found that $K_{p315.16^\circ} = 1.004$, corresponding to contents of 50.01% of cis- and 49.99% of trans-piperylene in the mixture. In view of the fact that, with rise in temperature right up to 1500° K, the difference in the values of ΔZ for the piperylene isomers remains almost constant -- not more than 200-300 cal/mole -- the equilibrium constant tends to the value of unity. It follows that, at almost all temperatures, the equilibrium mixture should contain equal amounts of the two forms, and not greatly differing amounts as found by Frank and coworkers, who give the values: 87% of trans-form at 315.16° K and 55-60% at 873.16° K [1]. The temperature dependence of the logarithm of the equilibrium constant for the formation of cyclopentadiene is shown in Fig. 1.

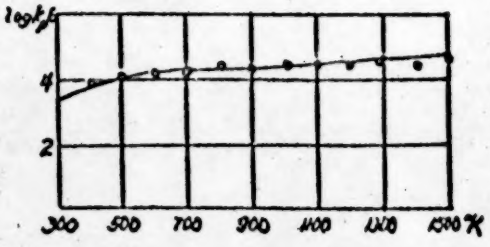


Fig. 1. Temperature dependence of the logarithm of the equilibrium constant for the formation of cyclopentadiene from piperylene.

As can be seen from Table 1 (see Experimental), whereas the yields of cyclopentadiene in the catalyzate vary greatly with temperature, attaining 50.4% at 650° over $Al_2O_3 + MnO$ (1:2), the actual extent of conversion of piperylene into cyclopentadiene does not exceed 18.5%. In a study of the kinetics of the cyclization of piperylene we established that the dehydrocyclization reaction is extremely slow. The rate constants of the reaction determined at 550° and 600° are $8.03 \cdot 10^{-5}$

and $5.41 \cdot 10^{-4}$ mole/cm, respectively. The activation energy is 59,105 cal/mole. With these values for the constants, the complete conversion of one mole of piperylene into cyclopentadiene at 600° in one hour will require a layer of catalyst about $1.8 \cdot 10^{5}$ cm in length and of unit cross section; alternatively, if the layer is of unit length the time required will be about the same. . It would appear that the obstacle to the attainment of thermodynamic equilibrium is the low rate of reaction, so that it should be possible to attain a greater degree of conversion by increase in the time of contact between piperylene and catalyst. However, as will be seen from the kinetic results represented in Fig. 2, the rate of formation of cyclopentadiene does not depend on the time of contact between piperylene and catalyst.

Fig. 2. Dependence of the rate of formation of cyclopentadiene from piperylene on the reciprocal of the space velocity

It follows from the data in Table 1 that, contrary to Kennedy and Hetzel's assertion [2], the yield of cyclopentadiene is dependent on the nature of the catalyst, so that the reaction is a catalytic one. This is particularly clear from the results of experiments with alumina-manganese oxide catalysts of various compositions. Whereas the yield of cyclopentadiene is greatly affected by the nature and composition of the catalyst, the extent of the conversion of piperylene into cyclopentadiene does not depend on the relative proportions of cis- and trans-forms present in the original piperylene, as can be seen from the data in Table 6.

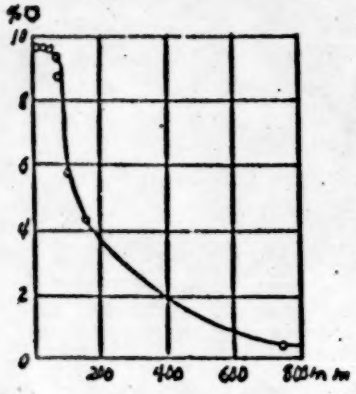


Fig. 3. Dependence of the yield of cyclopentadiene on pressure for the catalyst $Al_2O_3 + Cr_2O_3$ (1 : 1).

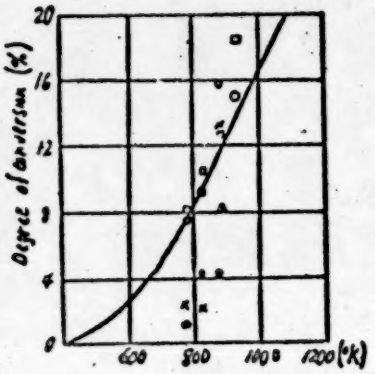
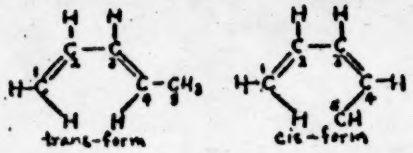


Fig. 4. Temperature dependence of the degree of conversion of piperylene into 1,4-pentadiene (calculated curve) and into cyclopentadiene (points corresponding to values obtained with the following catalysts: o) Zn_2SiO_4; □) $Al_2O_3 + MnO$ (1 : 2); Δ) $Al_2O_3 + Cr_2O_3$ (1 : 1); X) – Pt-aluminosilicate; •, Pt – SiO_2).

In one series of experiments (Table 7), the catalyzates, after removal of cyclopentadiene, were fractionated through a 30-plate column. In the piperylene-containing fraction, which boiled at 41.7-43.8°, the relative amounts of cis- and trans-piperylenes were determined from refractive index measurements. It was found that, irrespective of the composition of the original mixture of piperylenes, a mixture containing 42-50% of trans-piperylene was obtained, which is in close accord with the proportion that we calculated from thermodynamic data and is somewhat at variance with the results of Frank and coworkers [1]. The independence of the yield of cyclopentadiene on the composition of the original mixture of geometric isomers of piperylene and the catalytic character of the reaction enable us to conclude that in the process of forming cyclopentadiene piperylene is adsorbed on the catalyst in such a way that in the further act of transformation both the cis-form and the trans-form give intermediate states that are equivalent in energetic and steric respects. An examination of the spatial forms of the two isomers indicates that the molecule is most probably adsorbed at the 3-4 position.

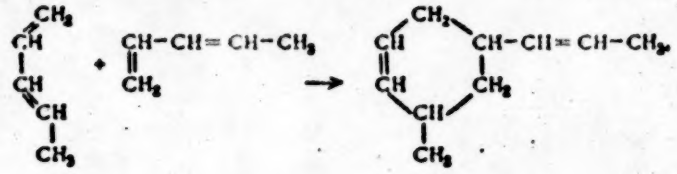


The interconversion of the two geometric forms is possible only when rotation around the 3-4 bond can occur, the removal of the high restraining potential barrier occurs as a result of the weakening or opening of the π-bond and the attachment of the piperylene to the catalyst at position 4.

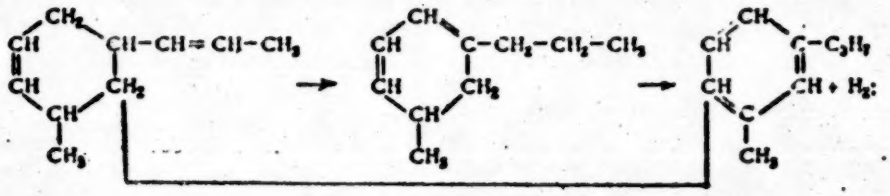
The pressure at which the reaction is carried out has a substantial effect on the yield of cyclopentadiene. As can be seen from the curve of Fig. 3 (plotted from the data in Table 7), at comparatively low pressures – up to about 70 mm – the yield of cyclopentadiene remains almost unchanged. With increase of pressure, however, the yield falls sharply, and at the same time the amount of cracking increases.

In experiments at atmospheric pressure, we isolated benzene, toluene, and o-xylene from the catalysis products. We consider that these hydrocarbons are formed as a result of secondary transformations of dimerization products of piperylene.

As shown earlier [5], piperylene dimerizes into 3-methyl-5-propenylcyclohexene:



which may then undergo dehydrogenation – either directly, or after isomerization into methylpropylcyclohexadiene – with formation of propyltoluene:



which, as a result of dealkylation and isomerization, probably yields the aromatic hydrocarbons that we found in the catalyzate. It must be noted that the cyclization of piperylene to cyclopentadiene is a complex process, which is accompanied by hydrogen-redistribution reactions, isomerization, polymerization, and cracking.

EXPERIMENTAL

Preparation of Catalysts

Pure and Mixed Oxide Catalysts [$Al_2O_3 + Cr_2O_3$ (1:1); $Al_2O_3 + MnO$ (1:1, 1:2, 1:4, 1:6); Al_2O_3, ZnO] were prepared from the corresponding nitrates by precipitation with 25% ammonia solution. They were washed free from nitrate, formed into cylinders, and dried at 150°. The alumina-manganese oxide catalysts were reduced, before being used in the experiments, by treatment with hydrogen in the catalysis tube with gradual increase in temperature to 600°, and then until water ceased to separate.

Zinc and Magnesium Silicates (Zn_2SiO_4, Mg_2SiO_4) were prepared by grinding separately prepared zinc and magnesium hydroxides with silica gel in a mortar. After the mixing, the catalysts were formed into cylinders and dried at 150°. Andalusite was ground mechanically into small particles and used without preliminary treatment.

TABLE 1

Cyclization of Piperylene to Cyclopentadiene at 25-30 mm

Expt. No.	Catalyst	Temperature (°C)	Space of velocity ($hour^{-1}$)	Cyclopentadiene content of catalyzate (%)	Extent of conversion into cyclopentadiene (%)	Extent of cracking (%)
1	$Pt-SiO_2$	500	0.5	1.3	1.1	12.0
2	Pt–aluminosilicate	500	0.006	3.0	2.2	33.0
3	Zn_2SiO_4	500	0.4	8.6	7.5	13.1
4	$Al_2O_3 + MnO$ (1 : 2)	500	0.5	9.1	8.1	12.2
5	$Pt-SiO_2$	550	0.5	5.3	4.1	22.5
6	Pt–aluminosilicate	550	0.16	2.3	2.0	16.0
7	Zn_2SiO_4	550	0.5	10.2	9.1	12.7
8	$Al_2O_3 + MnO$ (1 : 2)	550	0.5	12.1	10.5	13.0
9	$Al_2O_3 + MnO$ (1 : 4)	550	0.5	1.1	0.9	13.5
10	$Pt-SiO_2$	600	0.5	5.4	4.1	25.0
11	Pt–aluminosilicate	600	0.2	23.0	13.1	24.0
12	Pd–charcoal	600	0.5	10.7	7.3	32.0
13	Active charcoal	600	0.5	6.5	5.6	15.0
14	Zn_2SiO_4	600	0.5	21.9	15.9	15.0
15	ZnO	600	0.5	0.6	0.2	34.5
16	Mg_2SiO_4	600	0.5	9.9	7.1	28.0
17	Al_2O_3	600	0.5	1.4	0.9	37.0
18	$Al_2O_3 + Cr_2O_3$ (1 : 1)	600	0.5	9.7	8.1	15.4
19	$Al_2O_3 + MnO$ (1 : 1)	600	0.5	6.9	3.6	54.5
20	$Al_2O_3 + MnO$ (1 : 2)	600	0.5	21.7	12.8	43.7
21	$Al_2O_3 + MnO$ (1 : 4)	600	0.5	2.3	1.6	32.0
22	$Al_2O_3 + MnO$ (1 : 6)	600	0.5	4.6	2.5	21.0
23	$Al_2O_3 + TiO_2$ (1 : 19)	600	0.5	3.5	2.0	12.5
24	Andalusite	600	0.5	5.9	5.4	10.0
25	Zn_2SiO_4	650	0.5	32.9	15.0	54.4
26	$Al_2O_3 + MnO$ (1 : 2)	650	0.5	50.4	18.5	62.0

TABLE 2

Products of Contact-catalysis Reactions of Piperylene

Expt. No.	Catalyst	Properties of head fraction (up to 41.7°)				Properties of piperylene fraction (41.7-43.8°)			Content of residue (%) by volume
		B.p. (°C, corrected)	d_4^{20}	n_D^{20}	Content (% by volume)	d_4^{20}	n_D^{20}	Content (%) by volume)	
1, 5 and 10	$Pt-SiO_2$	26-41.7	0.6628	1.3983	17.3	0.6821	1.4275	67.9	13.4
2, 6 and 11	Pt–aluminosilicate	27.5-41.7	0.6701	1.4010	10.7	0.6829	1.4331	75.3	8.7
12	Pd–charcoal	18-41.7	0.6680	1.3955	15.5	0.6834	1.4329	73.5	11.1
13	Active charcoal	22-41.7	0.6674	1.3947	14.2	0.6831	1.4330	80.2	5.4
3, 7, 14 and 25	Zn_2SiO_4	34.3-41.7	0.6915	1.4122	5.9	0.6828	1.4330	75.4	17.7
18	$Al_2O_3 + MnO$ (1 : 1)	30-41.7	0.6884	1.4085	4.8	0.6830	1.4330	84.4	8.9
4, 8, 20 and 26	$Al_2O_3 + MnO$ (1 : 2)	27.0-41.7	0.6718	1.4015	7.4	0.6829	1.4331	81.7	10.3
9 and 21	$Al_2O_3 + MnO$ (1 : 4)	26.3-41.7	0.6640	1.3975	12.9	0.6824	1.4325	76.7	9.0
22	$Al_2O_3 + MnO$ (1 : 6)	26.0-41.7	0.6615	1.3960	16.0	0.6825	1.4325	73.0	9.7
18	$Al_2O_3 + Cr_2O_3$ (1 : 1)	26.0-41.7	0.6630	1.3970	20.1	0.6828	1.4325	77.1	12.5
23	$Al_2O_3 + TiO_2$ (1 : 19)	26.5-41.7	0.6693	1.3992	14.7	0.6836	1.4339	73.1	11.8
16	Mg_2SiO_4	29-41.7	0.6720	1.4031	8.4	0.6812	1.4307	72.1	18.2
24	Andalusite	27.3-41.7	0.6712	1.3997	4.3	0.6828	1.4332	88.2	5.9
17	Al_2O_3	29.4-41.7	0.6893	1.4075	4.7	0.6824	1.4329	85.9	8.3
15	ZnO	30.1-41.7	0.6892	1.4080	6.2	0.6817	1.4328	84.7	7.9

• The numbering is the same as in Table 1.

TABLE 3

Products Isolated after the Bromination of the Head Fractions (B.p. up to 41.7°)

Expt. No.	Paraffin part				Solid bromo compounds	
	B.p. (°C, corrected)	d_4^{20}	n_D^{20}	Volume (ml)	I (m.p. in °C)	II (m.p. in °C)
1, 5 and 10	27.3-36.5	0.6270	1.3581	2.3	84.6	116
2, 6 and 11	27.5-37.1	0.6283	1.3585	1.2	86.3-86.5	116
3, 7, 14 and 25		none present			–	116
4, 8, 20 and 26	27.2-37.4	0.6266	1.3579	1.3	–	116

TABLE 4

Liquid Bromo Compounds Isolated from the Products of the Bromination of the Head Fractions (B.p. up to 41.7°) of the Catalyzates from Experiments 1, 2, 5, and 7

B.p. of fraction / Expt. No.	55-60° (12 mm)		60-65° (12 mm)		65-70° (12 mm)		Above 70° (mm)
	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	n_D^{20}
1	1.6712	1.5101	1.6772	1.5093	1.6752	1.5112	1.5135
2	1.6710	1.5092	1.6781	1.5107	1.6760	1.5107	1.5140
5	1.6707	1.5090	1.6790	1.5105	1.6759	1.5110	1.5137
7	1.6715	1.5098	1.6782	1.5110	1.6762	1.5106	1.5160

TABLE 5

Data from the Literature for the Properties of Dibromopentanes

Dibromopentane	B.p. (° C)	d_4^{20}	n_D^{20}	Literature reference
2,3-Dibromo-2-methylpentane	56-58 (12)	1.6717	1.5112	[7]
1,2-Dibromopentane	58-60 (10-11)	1.6708	1.5088	[8]
2,3-Dibromo-4-methylpentane	65-66 (12)	–	–	[9]
2,3-Dibromopentane	58-58.5 (12)	1.6821	1.5099	Determined by us

TABLE 6

Catalytic Transformations of Various Mixtures of cis- and trans-Piperylenes (Space Velocity 0.5 hour^{-1})

Expt. No.	Catalyst	Original piperylene		Cyclopentadiene content of catalyzate (%)	Piperylene isolated from catalyzate	
		n_D^{20}	Content of trans form. (%)		n_D^{20}	Content of trans form (%)
1	Al_2O_3 + MnO (1:2)	1.4310	83.3	20.4	1.4332	46.7
2	Al_2O_3 + MnO (1:2)	1.4330	50.0	21.7	1.4335	41.7
3	Zn_2SiO_4	1.4325	57.0	21.9	1.4330	50.0
4	Zn_2SiO_4	1.4344	27.0	21.0	1.4333	45.0

Finely Dispersed Platinum and Palladium on Carriers were prepared from palladous and platinic chlorides, in the form of solutions absorbed in activated charcoal and commercial aluminosilicate catalyst, by reduction in the cold with formalin and alkali. These catalysts contained 5% Pd (on charcoal) and 6% Pt (on aluminosilicate).

Platinum on Silica Gel was prepared by the calcination of 150 ml of silica gel impregnated with a solution of 7 g of platinic chloride in 50 ml of water, with subsequent reduction with hydrogen at 300°. The catalyst contained 4% Pt.

Apparatus, Experimental Procedure, and Analysis of Catalyzates

Experiments on the reactions of piperylene were carried out in a quartz tube, 18 mm in diameter, in a

continuous-flow system. The temperature was measured with a chromel-alumel thermocouple. In a normal experiment, piperylene was passed to the reaction zone from an automatic buret, and in the kinetic measurements the supply was effected with the aid of a cylinder of about 100 ml capacity which we constructed; this was attached to the catalysis tube by a ground joint. The cylinder contained a spiral heated by an electric current supplied from a stabilized source of potential difference. The rate of supply of material was determined from the value of the current passing through the spiral. For each experiment, 20-80 g of piperylene was taken. All of the experiments, except one, were carried out in a vacuum. The reaction products were collected in a receiver cooled with water and in a series of three traps, two of which were immersed in a mixture of dry ice and methanol, and the third in liquid nitrogen. The gases that condensed in the last trap were mainly C_3-C_4 unsaturated hydrocarbons and methane. Immediately after the experiment, the liquid catalyzate was analyzed for cyclopentadiene by Afanasyev's method [6]. The results of the experiments are given in Table 1.

TABLE 7

Dependence of the Yield of Cyclopentadiene on Pressure in the Reactions of Piperylene over $Al_2O_3 + Cr_2O_3$ (1:1)

Expt. No.	Pressure (mm)	Cyclopentadiene content of catalyzate (%)	Residue (B.p. > 44°)		Extent of cracking (%)
			Weight (g)	Fraction of catalyzate (%	
1	10	9.7	3.7	10.1	15.4
2	30	9.7	3.7	10.5	17.8
3	50	9.6	3.9	12.1	36.5
4	70	9.4	4.0	13.5	37.4
5	90	8.9	4.2	13.8	38.0
6	100	5.7	4.2	14.1	39.0
7	150	4.3	4.5	14.3	43.7
8	760	0.4	4.7	14.0	57.5

TABLE 8

Dependence of the Yield of Cyclopentadiene on the Time of Contact with Platinum-Aluminosilicate Catalyst

Expt. No.	Temperature, °C	Supply of piperylene (mole/hour)	Rate of formation of cyclopentadiene (mole/hour)	Degree of conversion (as a fraction)	Rate constant (mole/cm)
1	600	0.910	0.0099	0.022	0.000500
2	600	0.667	0.0120	0.037	0.000601
3	600	0.576	0.0107	0.040	0.000577
4	600	0.397	0.0100	0.052	0.000501
5	600	0.197	0.0107	0.102	0.000500
6	600	0.910	0.0110	0.024	0.000545
7	600	0.667	0.0107	0.034	0.000567
8	550	0.164	0.0031	0.019	0.0000777
9	550	0.197	0.0035	0.018	0.0000812
10	550	0.164	0.0033	0.020	0.0000820

After cyclopentadiene had been determined, the catalyzates were distilled over sodium hydrogen sulfate through a 30-plate column with full return of reflux for three hours. In the course of this treatment the cyclopentadiene dimerized completely. The catalyzates from different experiments with a given catalyst were united and distilled through a 70-plate column. In all cases this resulted in a head fraction (b.p. up to 41.7°), a piperylene fraction (b.p. 41.7-43.8°), and a residue containing cyclopentadiene dimer and other condensation products. The relative amounts and the properties of the individual fractions are given in Table 2.

Combined head fractions from Experiments No. 1, 5, and 10; 2, 6, and 11; 3, 7, 14, and 25; 4, 8, 20, and 26 were brominated in acetic acid. The products were washed and dehydrated, and unchanged saturated hydrocarbons were then distilled off from a water bath. The bromo compounds were cooled and separated into solid and liquid fractions. The solid bromo compounds were fractionally crystallized from petroleum ether and alcohol, and the liquid bromo compounds were vacuum-distilled. The results obtained are given in Tables 3 and 4.

The properties indicate that pentane and isopentane occurred in the paraffin part, and 1,2,4,5-tetrabromopentane (I) and 1,2,3,4-tetrabromopentane (II) occurred among the solid bromo compounds.

Comparison with the constants in Table 5 indicates that our bromination products are mixtures of dibromopentanes. Hence, in the catalytic transformations of piperylene, the formation of cyclopentadiene is accompanied by the formation of pentanes and pentenes as a result of the redistribution of hydrogen. The effect of the relative proportions of the cis- and trans-forms of piperylene is shown in Table 6. In each of the four experiments we took a fresh portion of catalyst (50 ml) and 40 g of piperylene, in which the relative amounts of the cis- and trans-isomers were varied. The samples of piperylene were obtained by the fractionation of commercial piperylene through a 70-plate column. The experiments were carried out at 600°. The composition of the mixture was determined from its refractive index.

Dependence of the Yield of Cyclopentadiene on Pressure in the Reactions of Piperylene in Contact with $Al_2O_3 + Cr_2O_3$ (1 : 1)

The experiments were carried out at various pressures at a constant space velocity of 0.5 hour^{-1} at 600°. In each experiment we took a fresh portion of catalyst (50 ml) and 80 g of piperylene having n_D^{20} 1.4310. The cyclopentadiene content of the catalyzate was determined, and the catalyzate was then fractionated through a 30 plate column to separate the part boiling up to 44°. The residue was distilled from a Favorsky flask. The results obtained are given in Table 7.

After removal of unsaturated hydrocarbons by treatment with 80% sulfuric acid, the residue from Experiment 8 (b.p. 44-160°) was found to contain benzene, toluene, and o-xylene.

Dependence of the Yield of Cyclopentadiene on the Time of Contact with Platinum-Aluminosilicate Catalyst (6% Pt)

In order to avoid any distortion of results by reduction in activity, before the experiments wer commenced the sequence of oxidation by air and reduction by hydrogen under regeneration conditions was carried out twice. The amount of catalyst was the same (100 ml) in each experiment, and the amount of piperylene (n_D^{20} 1.4330) varied in different experiments from 5 to 60 g. The results of the experiments were used for the calculation of rate constants from Panchenkov's equation for the kinetics of a reaction occurring in a continuous system [10], the particular case taken being that of strong adsorption:

$$k = \frac{nx}{l},$$

in which k is the rate constant, n is the number of moles of piperylene passing into the reaction zone in unit time, x is the degree of conversion, and l is the length of the reaction zone filled with catalyst – in our case 40 cm. The experimental conditions and the values of the constants are given in Table 8. At 600° and space velocities of 0.06 and 0.1 hour^{-1}, the amounts of cyclopentadiene formed were 0.00852 and 0.0115 mole, respectively, the degrees of conversion being 0.138 and 0.117 (Fig. 2). The average values of the constants were determined: for 550° K $8.03 \cdot 10^{-5}$ mole/cm, and for 600° K $5.41 \cdot 10^{-4}$ mole/cm. Substitution of these values in the Arrhenius equation yielded a value of 59,105 cal/mole for the activation energy; since the adsorption is strong, the activation energy is true activation energy.

Mechanism of the Formation of Cyclopentadiene

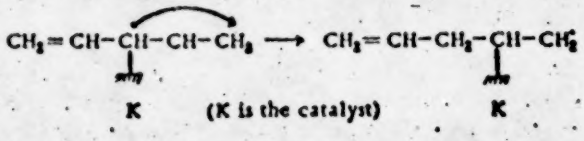
The only reported suggestion regarding the mechanism of the cyclization of piperylene was made quite recently [2]. According to this, the reaction goes in two stages:

$$CH_2=CH-CH=CH-CH_3 \longrightarrow CH_2=CH-CH=CH-CH_2^{\cdot} + H^{\cdot} \quad (1)$$

$$CH_2=CH-CH=CH-CH_2^{\cdot} \longrightarrow \begin{matrix} CH & CH \\ \| & \| \\ CH & CH \\ & CH_2 \end{matrix} + H^{\cdot};\ 2H^{\cdot} \longrightarrow H_2 \quad (2)$$

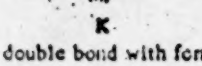
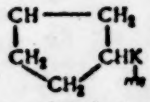
In the first stage a piperylene radical R$^{\cdot}$ and atomic hydrogen are formed. In order to form an idea of the actual mechanism of the reaction it is necessary to take into account the kinetic data concerning the reaction, the presence in the reaction products of pentanes and pentenes and the absence of cyclopentene, the catalytic character

of the reaction, the presence in the reaction products (in some experiments) of 1,4-pentadiene, and the occurrence of an upper limit for the yields of cyclopentadiene. On the basis of these data we consider that the reaction goes by a radical mechanism in three stages. In the first stage the piperylene molecule is adsorbed at the 3-4 position on the catalyst surface; as a result a valency is freed at the third carbon atom with formation of a radical, which isomerizes at the β-position, the free valency then passing to the fifth carbon atom:

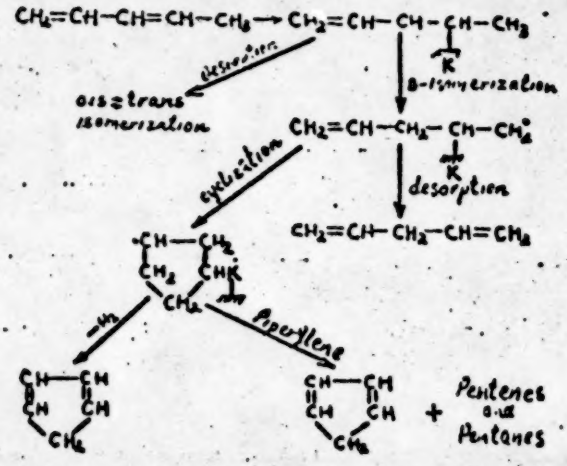


The secondary radical formed may not isomerize, but may be desorbed. This results in cis-trans conversion.

The β-isomerization of radicals has been observed by Voevodsky and Mardaleishvili [11] in a study of deuterium exchange in primary propyl and isobutyl radicals.

The heat of reaction of the first stage of formation and isomerization will be made up of the energy of the rupture of a π-bond (40-45 kcal) and the difference in the energies of bonds formed by hydrogen with a primary and with a secondary carbon atom (about 5 kcal). It will therefore be about 45-50 kcal/mole. On this basis, the activation energy will be 55-60 kcal/mole, which is in close accord with the experimental value (about 60 kcal). The radical  may be desorbed with formation of 1,4-pentadiene or may undergo intramolecular addition at the double bond with formation of a cyclic radical  (second stage). This stage proceeds with an insignificant activation energy. In the last (third) stage, redistribution of hydrogen between the radical formed in the second stage and piperylene occurs without the consumption of any activation energy; cyclopentadiene, pentenes, and pentanes are then formed. It is probable that to some extent cyclopentadiene is formed directly by dehydrogenation of the radical. The determining stage of the reaction is the first, since it occurs with the highest activation energy. As can be seen from the scheme of formation of the radical and its isomerization at the β-position, this process is analogous to the isomerization of piperylene into 1,4-pentadiene, so that the yield of cyclopentadiene will be determined by the thermodynamic equilibrium piperylene ⇌ 1,4-pentadiene. On the basis of the thermodynamic data of Kilpatrick and coworkers [3] we calculated the 1,4-pentadiene content of such an equilibrium mixture for various temperatures and plotted a curve for the dependence of the 1,4-pentadiene yield on temperature (Fig. 4). On the same diagram we marked the points corresponding to the yields of cyclopentadiene obtained at the same temperatures over various catalysts.

We thus obtain the following scheme for the formation of the transformation products of piperylene:



SUMMARY

1. The effects of various catalysts in the dehydrocyclization of piperylene to cyclopentadiene were investigated.

2. It was shown that the cyclization reaction is catalytic.

3. The activation energy of the process and the rate constants of the reaction at 550° and 600° were determined.

4. It was shown that the yield of cyclopentadiene does not depend on the relative amounts of the cis- and trans-forms present in the original piperylene, but depends on the pressure.

5. A mechanism is proposed for the cyclization reaction of piperylene.

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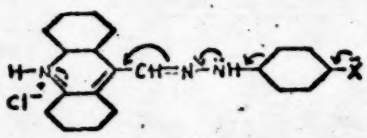
ABSORPTION SPECTRA AND MOLECULAR STRUCTURE

COMMUNICATION 4. EFFECT OF THE CHARACTER OF THE SUBSTITUENT ON COLOR IN DERIVATIVES OF 9-ACRIDINECARBOXALDEHYDE PHENYLHYDRAZONE HYDROCHLORIDE

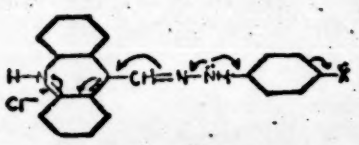
A. A. Kharkharov

Generalization of the widely known theoretical concepts and experimental data that have appeared in the literature on the relationship between color and structure in organic compounds enables us to conclude that the color of organic compounds depends primarily on the presence of electron-donating and electron-accepting centers in the molecule and on the number of interacting π-electrons (in particular, on the length of the conjugated chain). This conclusion is in close accord with the experimental data presented in this paper on the effect of the character of the substituent on color in para-substituted derivatives of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride.

As the length of the conjugated chain is almost constant in most of these compounds, the displacement in the principal absorption maximum should vary regularly with change in the electron-donating or electron-accepting properties of the substituent. Hence, the greater the tendency of the substituent to repel electrons:



the greater (other things being equal) should be its bathochromic effect and, on the other hand, the greater the tendency of the substituent to attract electrons:



the greater should be its hypsochromic effect. As is well known [1-5, 9], increase in the length of the conjugated chain is always accompanied by a displacement of the principal absorption maximum toward the longer waves, as will be shown below.

From the data in the table and in Fig. 1 on the absorption spectra of derivatives of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride it will be seen that the nitro group ($\Delta\lambda$ [illegible] $m\mu$) is the most powerful hypsochromic substituent. The reason for this lies in the fact that nitrogen, and particularly oxygen, attracts electrons more strongly than carbon does. The inductive displacement of electrons, therefore, will be directed from the benzene nucleus to nitrogen and oxygen, which will result in a reduction in the electron density of the carbon atoms of the benzene ring. The displacement of electrons in this direction is facilitated also by the presence of a coordinate link in the nitro group with positive charge on the nitrogen.

Finally, the oxygen of the nitro group is bound to nitrogen by a double bond. The π-electrons of this double bond interact with those of the benzene ring, and through them with the free pair of electrons on the hydrazone NH group, with formation of a unified electron cloud. As a result of a combination of all these effects, on all of

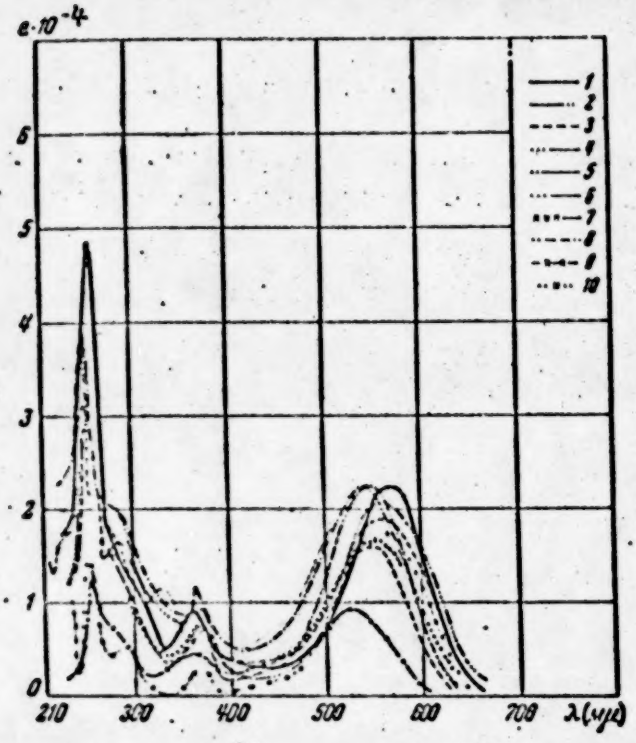


Fig. 1. Absorption spectra in alcoholic hydrogen chloride; 1) 9-acridinecarboxaldehyde phenylhydrazone; 2) 9-acridinecarboxaldehyde p-sulfamoylphenylhydrazone; 3) 9-acridinecarboxaldehyde p-acetylphenylhydrazone; 4) 9-acridinecarboxaldehyde p-formylphenylhydrazone; 5) 9-acridinecarboxaldehyde p-carboxphenylhydrazone; 6) 9-acridinecarboxaldehyde p-iodophenylhydrazone; 7) 9-acridinecarboxaldehyde p-chlorophenylhydrazone; 8) 9-acridinecarboxaldehyde p-bromophenylhydrazone; 9) 9-acridinecarboxaldehyde p-nitrophenylhydrazone; 10) 9-acridinecarboxaldehyde p-sulfophenylhydrazone.

the carbon atoms – particularly those in the ortho and para positions – a positive charge will appear, which, in its turn, will attract electrons from the NH group, i.e. will oppose the displacement of electrons in the direction from benzene nucleus to the acridine nitrogen [6].

The second among the substituents studied with respect to hypsochromic effect is the aldehyde group ($\Delta\lambda$ = – 23 mμ; see table and Fig. 1); its powerful electron-accepting properties are associated with the presence of an oxygen atom attached to carbon by a double bond. The oxygen strongly attracts electrons both by the induction mechanism (according to its position in the Mendeleev system), and also by the conjugation mechanism. The hydrogen of the aldehyde group, unlike the methyl of the acetyl group ($\Delta\lambda$ = – 22 mμ; see table and Fig. 1), does not lower the positive charge on the carbon atom appreciably. Replacement of the aldehyde group by hydroxyl, i.e. when we pass to carboxyl ($\Delta\lambda$ = 16 mμ; see table and Fig. 1), leads to quite an appreciable neutralization of the charge on the carbon and to a weakening of the electron-accepting properties of the group.

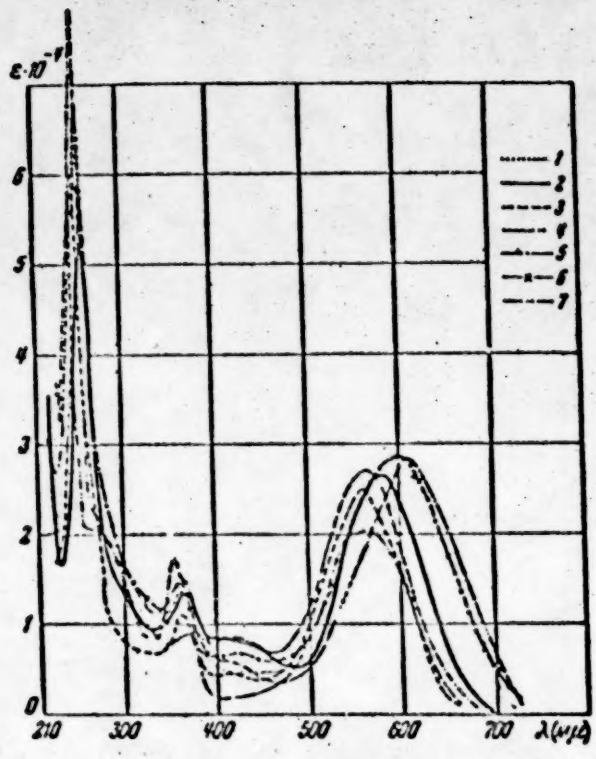
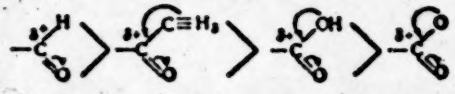


Fig. 2. Absorption spectra in alcoholic hydrogen chloride: 1) 9-acridinecarboxaldehyde p-methoxyphenylhydrazone; 2) 9-acridinecarboxaldehyde p-tolylhydrazone; 3) 9-acridinecarboxaldehyde phenylhydrazone; 4) 9-acridinecarboxaldehyde p-iodophenylhydrazone; 5) 9-acridinecarboxaldehyde p-thiocyanatophenylhydrazone; 6) 9-acridinecarboxaldehyde p-acetamidophenylhydrazone; 7) 9-acridinecarboxaldehyde p-ethoxyphenylhydrazone.

In the ionized state, the carboxyl group has a more feeble electron-accepting effect than it has in the nonionized state. The electron-accepting properties of carbonyl compounds fall in the sequence:



The electron-accepting power of a carbonyl-containing substituent is determined by the value of the positive charge (δ+) on the carbon of the carbonyl group. The value of this charge depends on the properties of the radicals attached to the carbonyl group. The more powerful the electron-donating effects of these radicals, the smaller the positive charge (δ+) remaining on the carbon of the carbonyl group and the weaker the electron-accepting properties of the substituent containing the carbonyl group.

Comparison between the hypsochromic effects of the sulfamoyl and sulfo groups ($\Delta\lambda = -22$ and -5 mμ, respectively; see table and Fig. 1) shows that the first of these has the stronger electron-accepting effect:

Comparison of the colors of internal salts of sulfonic acids in alcoholic solution with those of the sulfonic acids in hydrochloric acid solution showed that the absorption curves are identical, which indicates that in both cases the sulfo group is ionized. Both the sulfo and sulfamoyl groups contain hetero atoms having higher affinity for electrons than carbon has. Moreover, in these substituents the oxygen is bound to sulfur by a coordinate link. This should place the sulfo and sulfamoyl groups on the same level as the most strongly electron-attracting substituents. Their lower hypsochromic effects, however, stand in apparent contradiction to this conclusion. Closer examination removes this contradiction. These groups contain powerful electron-donating substituents: $-NH_3$ and $-O^-$. As $-O^-$ has the greater electron-repulsion effect, its neutralizing effect on the positive charge on the sulfur is greater than that of the $-NH_3$ group. We have shown by spectrum investigations on the sulfo and other groups that it is possible to determine whether a particular substituent is ionized under any given conditions.

The conjugation effect can be great not only for electron-donating substituents, but also for electron-accepting substituents, as can be seen from the effect of the group $-\overset{+}{N}H_3$ ($\Delta\lambda = 12$ mμ, see table). The positive charge of this substituent is very high, approximating numerically to that of the electron ($4.80 \cdot 10^{-10}$ esu), whereas the charge on the carbon of the aldehyde group, for example, is only a small fraction of this value. Also, unlike the aldehyde group, the $-\overset{+}{N}H_3$ group acts only by induction forces.

Whereas the octet of the carbonyl oxygen includes the pair of π-electrons of the carbon-oxygen bond, the ammonium nitrogen has an octet formed entirely by σ-bonds; it has no tendency to form a ten-electron shell, so that its interaction with the benzene ring is weaker than that of the carbonyl group; in this lies the source of the relatively weak hypsochromic effect of the $-\overset{+}{N}H_3$ group.

The experimental data that we have examined shows that the greatest displacement of the principal absorption maximum is found for substituents that show the maximum interaction with the π-electrons of the conjugated system. The groups that interact only by means of Coulomb forces have a more feeble effect. In halogen derivatives, the induction forces, which are directed from the benzene ring to the substituent, lead to a reduction in the electron densities of the carbon atoms of the aromatic residue; these forces are opposed by conjugation forces arising from the interaction of the free pair of electrons of the halogen with the π-electrons of the benzene ring.

The examples of the hypsochromic effects of chlorine ($\Delta\lambda = -8$ mμ; see table and Fig. 1) and bromine ($\Delta\lambda = -2$ mμ; see table and Fig. 1) show particularly clearly that the electron displacement occurs in the direction of the element belonging to the higher group of the periodic system and that within a given group of the periodic system the atom having the lower volume has the more pronounced electron-donating character.

As a result of the great difference in charge between carbon and chlorine, the inductive hypsochromic effect of chlorine predominates over its conjugative bathochromic effect. However, for iodine substituted in the para position ($\Delta\lambda = +2$ mμ; see table and Fig. 2), the reverse effect is observed. Here the conjugative bathochromic effect suppresses the inductive hypsochromic effect. An accumulation of quantitavtive changes results in a qualitative change. As a rule, substituents having a free pair of electrons on the atom that is directly attached to the aromatic nucleus have bathochromic effects. Some substituents of this sort (amino and hydroxy groups, and their derivatives), as already noted above, have been called auxochromes. The example of the halogens shows that this situation is maintained only when the conjugative forces are more powerful than the inductive forces.

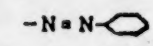
The group $-\overset{\frown}{S}-\overset{\frown}{C}\equiv N$ ($\Delta\lambda = -3$ mμ; see table and Fig. 2) can be regarded as a combination of two substituents: as a thiol group in which the hydrogen has been replaced by a nitrile group. The thiol group has an unshared electron pair and is to be regarded as an auxochromic group: its bathochromic effect is not less than that of the hydroxy group. On the contrary, the nitrile group is one of the most powerful electron-accepting substituents. For example, the dipole moment of the nitrile group is between those of the nitro and aldehyde groups. The behavior of the $-S-C\equiv N$-group is very reminiscent of that of the halogens. The nitrile group neutralizes the electron-donating character of the sulfur almost completely, so that the $-S-C\equiv N$-group is found to have only a very weak bathochromic effect.

The examples that we have analyzed show that a molecule taken as a whole, and also an individual substituent, should be regarded as a dialectical unity of opposites, as a unity of attractive and repulsive forces.

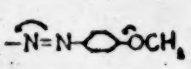
In the groups $-CH=N-NH-$⬡ ($\Delta\lambda = +8$ mμ, see table) and $-\overset{\|}{\underset{\|}{N}}-$⬡ ($\Delta\lambda = +17$ mμ, see table)—like the $-S-CN$ group and iodine atom, and most of the other bathochromic substituents — conjugation forces predominate over induction forces. In this case we have a substituent containing a double bond, which acts bathochromically by lengthening the conjugated chain [2]. This bathochromic effect readily hides any hypsochromic

effect associated with a displacement of electrons from the benzene nucleus to the nitrogen atoms of the azo group (on account of the position of nitrogen in the periodic system).

The further deepening of color from phenylazo ($\Delta\lambda = +17$ mμ, see table) [6]:

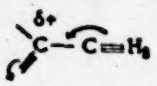


to p-methoxyphenylazo ($\Delta\lambda = +28$ mμ, see table)



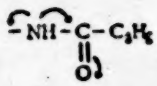
is to be associated with the inclusion of the OCH_3 group in the conjugated chain.

The methyl group ($\Delta\lambda = +18$ mμ, see Fig. 2 and table)

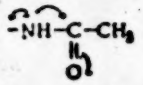


has a bathochromic effect as a result of the marked conjugation of σ, π -electrons [7, 8]. It is an electron-donating substituent and assists the acridinium nitrogen to change the electron densities of all the atoms of the system, with the participation of the free electron pair of the $-NH-$ group.

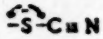
The benzamido group ($\Delta\lambda = 34$ mμ):



and the acetamido group ($\Delta\lambda = 36$ mμ; see Fig. 2 and table):

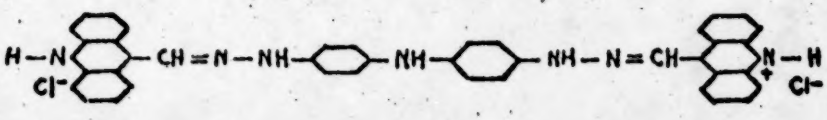


like the thiocyanato group:



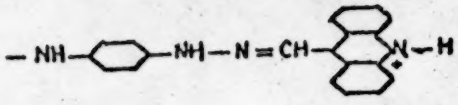
are combinations of pairs of substituents: the amino group and the benzoyl or acetyl group. The amino group contains an unshared pair of electrons and is one of the most powerful electron-donating groups; more powerful, in fact, than the thiol group. On the other hand, benzoyl and acetyl have marked electron-accepting properties. They are however weaker in this respect than the nitrile group, so that the electron-donating properties of the benzamido and acetamido groups are considerably more marked than those of the thiocyanato group. Correspondingly, there is a much greater displacement of the absorption maximum ($\Delta\lambda$) for 9-acridinecarboxaldehyde p-benzamido- and p-acetamido-phenylhydrazones (as hydrochlorides) than for the corresponding p-thiocyanatophenylhydrazone.

Nevertheless, the acid residues reduce the electron-donating effect of the amino group to such an extent that its bathochromic effect becomes less than that of the hydroxyl group ($\Delta\lambda = 48$ mμ). We meet a similar phenomenon in the case of bis (9 acridinecarboxaldehyde) (iminodi -p-phenylene) dihydrazone dihydrochloride ($\Delta\lambda = -2$ mμ; see table and Fig. 3):



This compound can be regarded as the salt of the cation of 9 acridinecarboxaldehyde phenylhydrazone containing an amino substituent the hydrogen of which is replaced by a residue of a 9-acridinecarboxaldehyde phenylhydrazone cation.

The substituent:



has powerful electron-accepting properties, and it attracts the free electron pair so strongly that the substituted amino group must be regarded, like chlorine, as an electron-accepting substituent, in spite of its free electron pair.

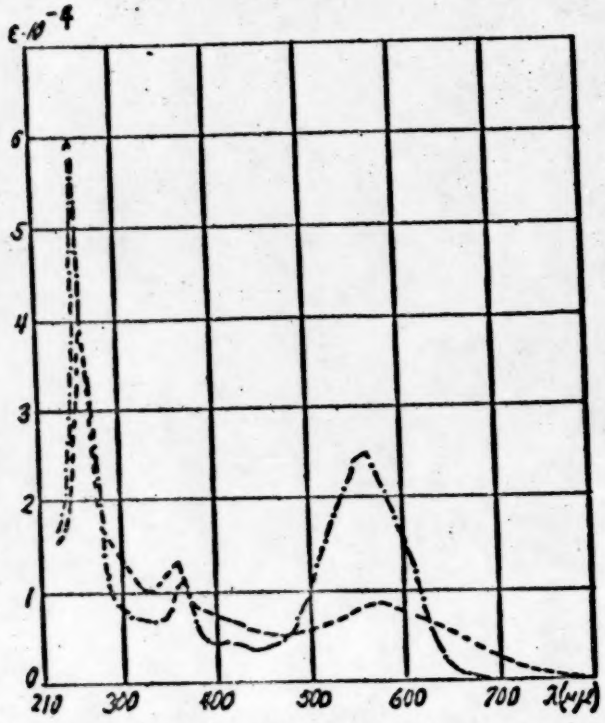
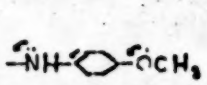


Fig. 3. Absorption spectra in alcoholic hydrogen chloride: — · — · bis (9-acridinecarboxaldehyde) (iminodi-p-phenylene) dihydrazone; — — — 9-acridinecarboxaldehyde phenylhydrazone

In groups –OH ($\Delta\lambda$ = +48 mμ; see table), $-OCH_3$ ($\Delta\lambda$ = +48 mμ; see Fig. 2 and table), and $-OC_2H_5$ ($\Delta\lambda$ = +48 mμ; see Fig. 2 and table), the negative effect of the induction forces is more than overcome by conjugation forces, and it is the relation between these two kinds of forces that determines the positions of these groups among bathochromic substituents.

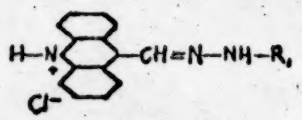
The identity in the values of the displacement of the principal absorption maximum of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride due to the introduction of a hydroxyl, a methoxyl, and an ethoxyl group indicates that under the conditions of measurement the hydroxyl group is in the unionized state. The difference in the effects of hydrogen and alkyl is so slight that we were unable to detect it.

All that we have said about the above substituents can be extended to anilino ($\Delta\lambda$ = 93 mμ, see table) $-NHC_6H_5$ and to p-anisidino ($\Delta\lambda$ = 153 mμ, see table):



TABLE

Displacement of the Principal Absorption Maximum in Derivatives of 9-Acridinecarboxaldehyde Phenylhydrazone Hydrochloride



containing a Substituent in the para-Position to the NH Group

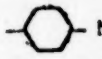
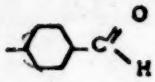
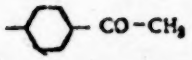
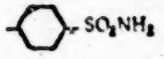
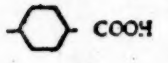
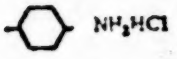
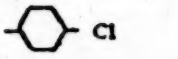
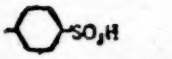
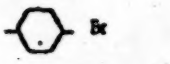
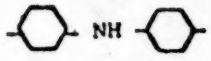
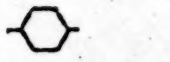
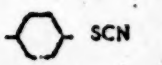
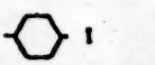
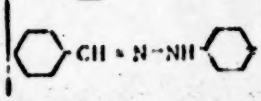
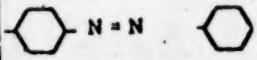
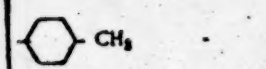
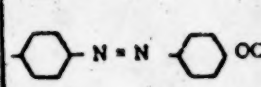
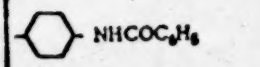
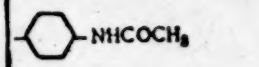
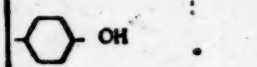
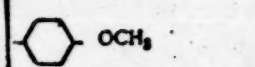
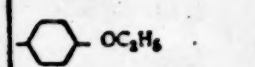
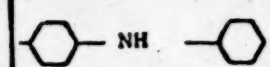
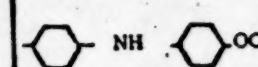
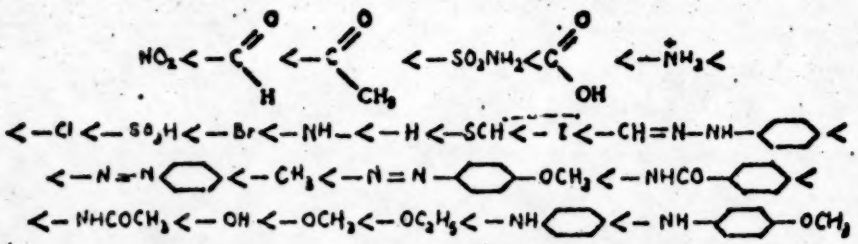
Number	Name of substance	R	Long-wave absorption maximum (mμ)	Displacement of absorption maximum Δλ (mμ)
1	9-Acridinecarboxaldehyde p-nitrophenylhydrazone hydrochloride		522	−40
2	9-Acridinecarboxaldehyde p-formylphenylhydrazone hydrochloride		539	−23
3	9-Acridinecarboxaldehyde p-acetylphenylhydrazone hydrochloride		540	−22
4	9-Acridinecarboxaldehyde p-sulfamoylphenylhydrazone hydrochloride		540	−22
5	9-Acridinecarboxaldehyde p-carboxyphenylhydrazone inner salt		546	−12
6	9-Acridinecarboxaldehyde p-aminophenylhydrazone dihydrochloride		550	−12
7	9-Acridinecarboxaldehyde p-chlorophenylhydrazone hydrochloride		554	− 8
8	9-Acridinecarboxaldehyde p-sulfophenylhydrazone inner salt		557	− 5
9	9-Acridinecarboxaldehyde p-bromophenylhydrazone hydrochloride		560	− 2
10	Bis(9-Acridinecarboxaldehyde)(iminodi-p-phenylene)dihydrazone dihydrochloride		560	− 2
11	9-Acridinecarboxaldehyde phenylhydrazone hydrochloride		562	0
12	9-Acridinecarboxaldehyde p-thiocyanatophenylhydrazone hydrochloride		565	3
13	9-Acridinecarboxaldehyde p-iodophenylhydrazone hydrochloride		566	4
14	9-Acridinecarboxaldehyde a-(phenylhydrazono)-p-tolylhydrazone hydrochloride		570	8

TABLE (continued)

Number	Name of substance	R	Long-wave absorption maximum (mμ)	Displacement of absorption maximum Δλ (mμ)
15	9-Acridinecarboxaldehyde p-phenylazophenylhydrazone hydrochloride		579	17
16	9-Acridinecarboxaldehyde p-tolylhydrazone hydrochloride		580	18
17	9-Acridinecarboxaldehyde p-(p-methoxyphenylazo)phenylhydrazone hydrochloride		590	28
18	9-Acridinecarboxaldehyde p-benzamidophenylhydrazone hydrochloride		596	34
19	9-Acridinecarboxaldehyde p-acetamidophenylhydrazone hydrochloride		598	36
20	9-Acridinecarboxaldehyde p-hydroxyphenylhydrazone hydrochloride		610	48
21	9-Acridinecarboxaldehyde p-methoxyphenylhydrazone hydrochloride		610	48
22	9-Acridinecarboxaldehyde p-ethoxyphenylhydrazone hydrochloride		610	48
23	9-Acridinecarboxaldehyde p-anilinophenylhydrazone hydrochloride		655	93
24	9-Acridinecarboxaldehyde p-(p-anisidino)phenylhydrazone hydrochloride		715	153

The exceptionally high bathochromic effects of these substituents are associated with the fact that their entry into the dye molecule is accompanied by considerable lengthening of the conjugated chain and by marked electron-donating properties.

Thus, the effects of all of the substituents that we have investigated can be arranged in the following sequence (see table):



This sequence, which is derived from experimental results, is in accord with the concepts regarding the structures and properties of organic molecules that have been developed by Soviet chemists.

EXPERIMENTAL

The spectrum investigations were carried out with an SF-1 photoelectric spectrophotometer over the range 210-800 mμ. The solvent used was 0.2 N alcoholic hydrogen chloride. Effects due to solvent were excluded. In the spectrum measurements, all of the dyes were used at the same concentration. All of the substances were prepared under the conditions used previously for the preparation of 9-acridinecarboxaldehyde phenylhydrazone; their purities were checked by their nitrogen contents, determined by combustion. The results of the spectrum investigations are given in Figures 1, 2, and 3 and in the table. More detailed information about the compounds discussed in this paper will be given in a future communication.

SUMMARY

1. It is shown that the presence of a substituent in the phenyl nucleus of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride has a very great influence on its color.

2. A study of the absorption spectra of these compounds provides convincing evidence that the color of organic substances depends essentially on the presence of electron-donating and electron-accepting centers and on the number of interacting π-electrons (in particular, on the length of the conjugated chain). The more marked the opposing characters of the groups or atoms linked through the conjugated chain, the more powerful their bathochromic effect. On the other hand, the greater the electron-accepting power of the substituent in the phenyl group of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride, the greater its hypsochromic effect. Increase in the length of the conjugated chain always acts bathochromically.

3. The absorption spectra of para-substituted phenylhydrazones of 9-acridinecarboxaldehyde hydrochloride were determined in the wavelength range 210-800 mμ, and the batho- or hypso-chromic effects of 22 substituents were determined

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IDENTIFICATION OF HYDROCARBONS WITH THE AID OF DISPERSION CURVES

I. V. Obreimov and T. N. Shkurina

Dispersion curves determined over a wide range of wavelengths can be used as criteria in the identification of organic substances. There have been only a few investigations on the determination of dispersion curves in the ultra-violet region of the spectrum. Systematic measurements over a wide range of wavelengths were first made by Anri [1] and Voellmy [2], who used the compensating prism method. These authors, unfortunately, do not give their primary data. Individual organic substances have been investigated by Allsopp [3] and by Lowry and Allsopp [4] by the interferometric method. The work of Friberg [5] is also of interest: he made dispersion measurements with the interferometer on the gaseous hydrocarbons methane, ethane, propane, butane, and ethylene.

EXPERIMENTAL

The refractive indices of the hydrocarbons investigated were determined over a wide range of wavelengths (6500-2500 A) by the Fresnel diffraction method [6, 7]. A parallel beam of white light was passed through a plate having plane parallel sides and immersed in the liquid. A part of the beam passed through the plate, and part through the liquid. Along the edge of the geometric shadow from the plate, the interference of the two beams was to be observed. The shadow of the edge of the plate fell on the slit of a spectrograph, and in the focal plane of the spectrograph the picture shown in Fig. 1 was to be observed.

The center of each dark spot corresponds to a wavelength for which $\underline{N}$ is equal to an odd number of half-waves, and the bright interval between spots corresponds to a wavelength for which N is a whole number. Integral values of $\underline{N}$ from $\underline{N}$ = 117 to $\underline{N}$ = 120 are indicated by dots. The refractive index $\underline{n}$ of 1,5-hexadiene increases more slowly than that of quartz. With further increase in frequency, the refractive index of 1,5-hexadiene increases more rapidly than that of quarts, and the numbers begin to decrease. There is a corresponding change in the slope of the diffraction spots.

By measuring the number of diffraction spots we can estimate the variation in the refractive indices of liquids. The refractive index was calculated according to the formula:

$$n_1 = n_q + \frac{N\lambda}{d}, \qquad (1)$$

in which n_1 is the refractive index of the liquid, n_q is the refractive index of the quartz, $\underline{N}$ is the number of the diffraction spot, λ is the wavelength, and $\underline{d}$ is the thickness of the standard quartz plate.

An ISP-22 spectrograph was used in the investigation. The source of ultraviolet radiation was provided by a super-high pressure krypton lamp. A diagram of the experimental arrangement is given in Fig. 2. The design of the cell is shown in Fig. 3. The standard quartz plate was fixed by means of a trace of fish glue to the inner surface of the quartz window of the cell. The thickness $\underline{d}$ of the plate was 1.0635 mm*.

The thickness of the layer of liquid between the windows of the cell was about 9 mm. The cell was fixed in front of the slit of the spectrograph on a special holder. This cell holder was pivoted, so that the plate could be placed strictly perpendicular to the beam from the collimator. Adjustment for perpendicularity was carried out by the autocollimation method.

If the diffracting edge of the block is parallel to the horizontal slit illuminated by the light source and perpendicular to the vertical slit of the spectrograph, then the diffraction picture (as shown in Fig. 1) will take the form

* The dispersion curve for the standard plate was determined jointly by the Kiev Institute of Physics of the Academy of Sciences of the Ukrainian SSR and the Institute of Organic Chemistry of the Academy of Sciences of the USSR; it will be published in the near future.

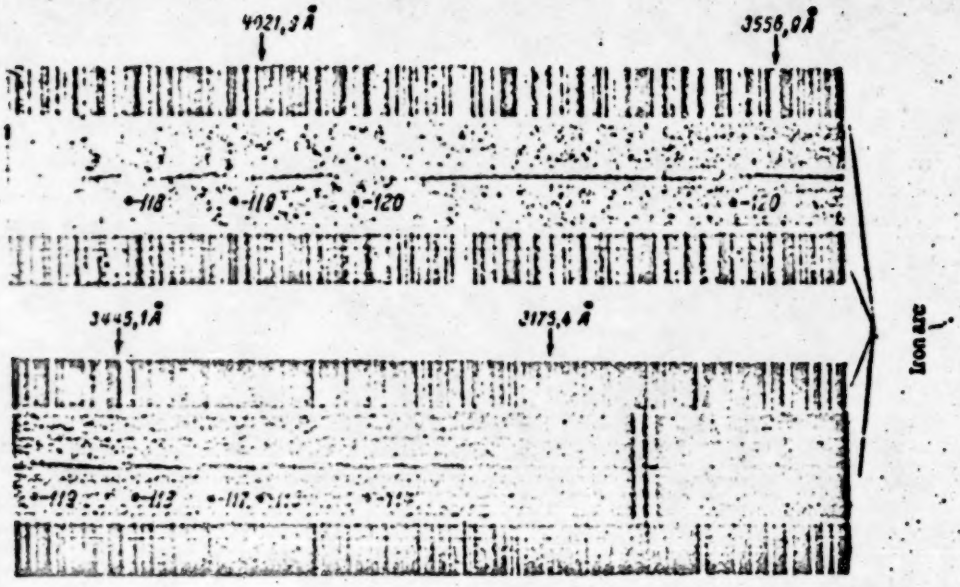

Fig. 1. Diffraction picture of 1,5-hexadiene-quartz.

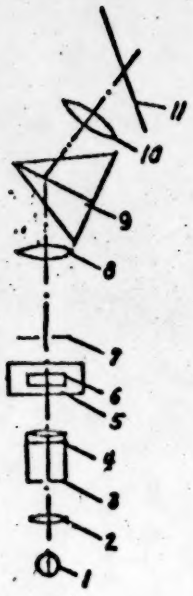

Fig. 2. Diagram of experimental arrangement: 1) light source; 2) quartz condenser; 3) collimator having an archromatic quartz-fluorite objective; 4) objective; 5) cell with plane windows for liquid under investigation; 6) quartz-glass plate having parallel plane sides; 7) slit of the ISP-22 spectrograph; 8 and 10) objectives; 9) prism; 11) photographic plate.

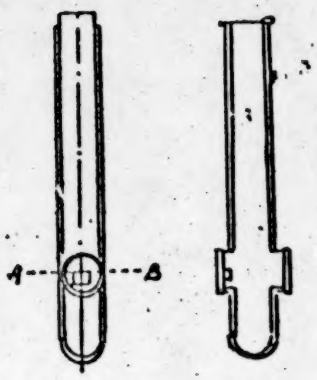

Fig. 3. Refractometric cell. The face AB of the standard plate is ground and polished in a plane strictly perpendicular to the parallel sides, and there are no bevels on the edges.

of drawn-out oval spots. Above and below in Fig. 1 the spectrum of the iron arc is shown. In the center will be seen the diffraction picture – drawn out into a spectrum – due to the side phase of the quartz block, which is here immersed in 1,5-hexadiene.

The number of the diffraction spot corresponding to $\lambda = 5893$ A was determined by direct calculation from the value of the refractive index obtained on an Abbe refractometer; n is then obtained accurate within $1 \cdot 10^{-4}$, and the whole dispersion curve will be accurate within not less than $1\text{-}2 \cdot 10^{-4}$.

Substances Investigated

The substances selected for investigation were saturated hydrocarbons having straight and branched chains, unsaturated hydrocarbons including compounds having conjugated double bonds, and cycloalkanes: 1) hexane, b.p. 68.7-68.8° (760 mm); d_4^{20} 0.6594; n_D^{20} 1.3751; 2) heptane, b.p. 98.3-98.4° (760 mm); d_4^{20} 0.6834; n_D^{20} 1.3878; 3) octane, b.p. d_4^{20} 0.7026; n_D^{20} 1.3974; 4) 2,2,4-trimethylpentane, b.p. 99.0-99.7° (760 mm), d_4^{20} 0.6908; n_D^{20} 1.3925; 5) 1-hexene, d_4^{20} 0.6734; n_D^{20} 1.3925; 6) 1-heptene, b.p. 92.8-92.9° (745 mm); d_4^{20} 0.6971; n_D^{20} 1.4001; 7) 1-octene, d_4^{20} 0.7160; n_D^{20} 1.4130; 8) 2,2,4-trimethylpentene (mixture 1- and 2-pentene derivatives), b.p. 102.4-102.8° (752 cm); n_D^{20} 1.4130; 9) cyclopentane, b.p. 49.5-49.8° (755.7 mm); d_4^{20} 7556; n_D^{20} 1.4063, 10) methylcyclopentane, b.p. 71.0° (737.8 mm); d_4^{20} 0.7465; n_D^{20} 1.4110; 11) 1,5-hexadiene, b.p. 59-60°; d_4^{20} 0.6915, n_D^{20} 1.4040; 12) isoprene, d_4^{20} 0.6806; n_D^{20} 1.4202; 13) mixture of dipentene and diprene, b.p. 173.8-174.8°; d_4^{20} 0.8436; n_D^{20} 1.4735; 14) alloocimene, b.p. 79° (11 mm); n_D^{16} 1.5450.

Hexane, heptane, octane, 2,2,4-trimethylpentane, 1-hexene, 1-heptene, and 1,5-hexadiene were obtained from the Catalytic-Synthesis Laboratory of the Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences, 2,2,4-trimethylpentene from the Pyrogenic-Processes Laboratory of the same institute, isoprene and the mixture of dipentene and diprene from the Unsaturated-Compounds Laboratory of the same institute, 1-octene, 2,2,4-trimethylpentene, cyclopentane, and methylcyclopentane from the Organic-Catalysis Laboratory of the same institute, and alloocimene from B. A. Arbuzov. To all those who provided these compounds we wish to express our warmest thanks.

Experimental Results

1. Temperature. The refractive indices of liquids are greatly dependent on temperature; for a change of temperature of about 1°, the refractive index of an organic liquid may be reduced by about $5 \cdot 10^{-4}$. For some liquids we measured the dispersion curve at two temperatures differing by 2-3°. It was found that dispersion curves for different temperatures can be brought into coincidence by the addition of a quantity that is the same for all

TABLE 1

Constants of the Dispersion Formula (2) for Different Aliphatic Hydrocarbons over the Wavelength Range 6500-2500 A

Substance	A	$B \cdot 10^{-9}$	$\nu_0^2 \cdot 10^{-9}$	γ_0 cm $\cdot 10^5$	Strength of oscillator f	Corrections
1	2	3	4	5	6	7
Methane *	–	–	9.638	1.04	1.24	–
Ethane *	–	–	9.355	1.07	1.97	–
Propane *	–	–	8.362	1.10	2.56	–
Hexane	1.2526	4.4702	7.2904	1.17	11	0
Heptane	1.1953	5.4594	7.7673	1.14	15	0
Octane	1.2683	4.7170	7.1614	1.18	13	0
2,2,4-Trimethylpentane	1.3228	3.8192	6.5211	1.24	12	0
Cyclopentane	1.2901	4.3816	6.6782	1.22	7.6	0
Methylcyclopentane	1.3281	3.7382	5.9407	1.30	7.8	0
Ethylene*	–	–	6.906	1.45	0.74	–
Propene*	–	–	3.716	1.49	0.90	–
1-Hexene	1.4019	2.3555	4.7815	1.45	5.5	0
1-Heptene	1.3831	2.7756	5.1135	1.40	7.3	0
1-Octene	1.4211	2.6875	4.9732	1.42	7.9	0
2,2,4-Trimethylpentene	1.4613	2.2327	4.5072	1.49	6.8	0
1,5-Hexadiene	1.4147	2.0910	4.0429	1.57	4.7	0
Dipentene-diprene mixture	1.5250	2.4491	4.0844	1.57	6.5	0
Isoprene	1.6057	2.8019	2.2406	2.11	1.5	C
Alloocimene	1.8650	0.5599	1.3813	2.67	1.8	C

* The data for the gaseous hydrocarbons - methane, ethane, propane, ethylene, and propene - are taken from Friberg's paper [5].

wavelengths, i.e. the two dispersion curves can be brought into coincidence by a parallel displacement. In other words, dn/dt is independent of λ (over the range 6500-2500 A). This result is confirmed by available data on the dependence of refractive indices of quartz glass on temperature [8]. In our further considerations all values of n will be reduced to 20°.

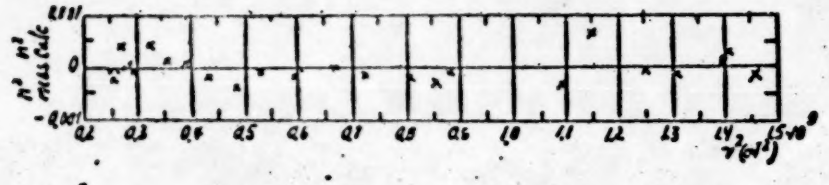

Fig. 4. Correction curve for 1-octene

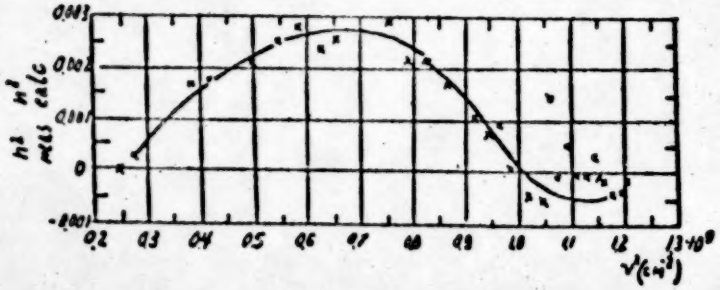

Fig 5. Correction curve for isoprene

2. Interpolation of Values of Refractive Index. Through all experimental values of n, interpolation curves based on a formula of the Sellmeier type were drawn; the formula has three constants:

$$n^2 = A + \frac{B}{\nu_0^2 - \nu^2} \qquad (2)$$

ν being the wave number, and A, B, and ν_0 constants. Data for the dispersions of the liquids studied are given in Table 1*.

3. Determination of Intermediate Values of n with the aid of Formula (2). As a result of measurements of n we obtain an enormous number of experimental points, and the recording of these would occupy a very large space. As there are no generally recognized rules for the recording of the results of dispersion measurements, we propose to use two methods. The first of these is to give a formula of type (2) together with correction curves. Figures 4, 5, and 6 give the correction curves for 1-octene, isoprene, and alloocimene. As will be seen from Fig. 4, formula (2) gives a close rendering of the course of the dispersion curve for 1-octene over the wavelength range 6500-2500 A, and it can be used directly for the calculation of values of n at intermediate wavelengths. Substances for which formula (2) can be used directly for determining intermediate values of n are indicated in the seventh column of Table 1 by the symbol 0.

TABLE 2

Refractive Indices of Hexane at 20°

λ (A)	$\nu = 1/\lambda^2$	n^2	n
6500	2,3669	1.8863	1.3734
6400	2,4414	1.8870	1.3737
6300	2,5195	1.8877	1.3739
6200	2,6015	1.8885	1.3742
6100	2,6874	1.8892	1.3745
6000	2,7778	1.8900	1.3748
5900	2,873	1.8909	1.3751
5800	2,973	1.8918	1.3754
5700	3,078	1.8928	1.3758
5600	3,189	1.8938	1.3761_5
5500	3,306	1.8949	1.3765_3
5400	3,429	1.8960	1.3769_3
5300	3,560	1.8972	1.3774
5200	3,698	1.8985	1.3778
5100	3,845	1.8999	1.3784
5000	4,000	1.9014	1.3789_3

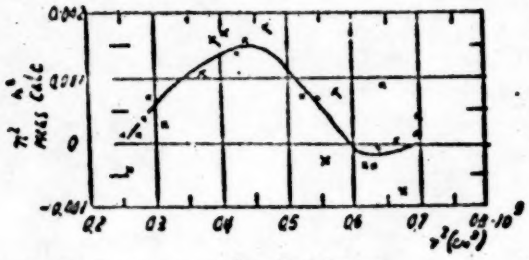

Fig. 6. Correction curve for alloocimene

Table 2 gives values of the refractive index of hexane calculated from formula (2) and the data in Table 1.

In order to obtain intermediate values of n for isoprene and alloocimene, it is necessary to use formula (2) with the addition of a correction taken from the curves of Figure 5 and 6. Substances for which a correction curve must be used in calculating n by formula (2) are indicated in Table 1 by the letter C. Hence, by the aid of Table 1 and the correction curves, the reader can compile a table of refractive indices for the wavelength range in which he is interested.

It will be seen from Figures 4, 5, and 6 that n^2 calculated from formula (2) and corrected as necessary, is obtained accurate within $\pm 5 \cdot 10^{-4}$. The second method is to give values of the refractive index for standard wavelengths. In the visible region of the spectrum we have the Fraunhofer lines C, D, F, and G', which are generally accepted as standards, and to these we propose to add the mercury wavelengths 4046.56, 3650.15, 3478.10, 3131.83, 2967.27, 2536.519, and 2482.8 A, which are often present in the light source. Table 3 shows this method of recording the dispersion curve.

4. Extrapolation of the Results. The interpolation formula (2) is Sellmeier's dispersion formula, which was deduced on the assumption that the dispersing medium is a gas having a single absorption band of frequency ν_0 and

* In a previous paper [7] we interpolated the value of the molecular refraction MR with the aid of Sellmeier's formula in order to enable us to collate our measurements with those of Voeliny. The values of f given there cannot, of course, be similar to those calculated in the present investigation; the calculations were done only in order to demonstrate that the values were high.

TABLE 3

Refractive Indices of Hexane Calculated for Standard Wavelengths from the Data of Table 1

Spectrum line	n	Spectrum line	n
C	1.3733_5	3650.15 A	1.3914_5
D	1.3751_5	3131.83 A	1.4019_5
F	1.3797	2967.28 A	1.4254_5
Q'	1.3834_5	2536.52 A	1.4254_5
4046.56 A	1.3863_5	2482.82 A	1.4297

the dispersion is measured in a region of the spectrum appreciably removed from ν_0, i.e. at a point at which absorption is low. The term A is associated with the effect of all the other absorption bands, which are considered to be even more far-removed than the band ν_0. The coefficient B in Sellmeier's formula is related to the effective strength of the oscillator of the ν_0 band by the formula:

$$B = f \frac{Ne^2}{\pi mc^2}, \qquad (3)$$

in which f is the effective strength of the oscillator, m is the mass of the electron, c is the velocity of light, e is the charge on the electron, and N is the number of molecules in

1 cc $= \frac{6.02 \cdot 10^{23}}{M} d$ (M is the molecular weight)

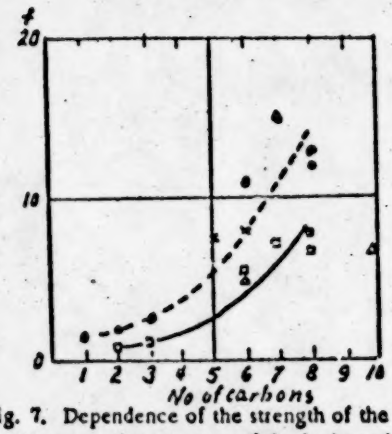

Fig. 7. Dependence of the strength of the oscillator on the structure of the hydrocarbon: • - saturated aliphatic hydrocarbons (Table 1); x - cycloalkanes; o - aliphatic hydrocarbons having one double bond; Δ - 1,5-hexadiene and dipentene-diprene mixture; □ - isoprene and alloocimene. The broken line is the curve representing the data for saturated hydrocarbons, and the continuous line is for unsaturated hydrocarbons having one double bond. The data for hydrocarbons having 1, 2, and 3 carbons are taken from Friberg's paper [5]

$$f = \frac{B \cdot M}{d} \cdot 1.85 \cdot 10^{-11}. \qquad (4)$$

in which d is the density of the substance. Values of f calculated in this way are given in Column 6 of Table 1.

5. Relation between the Constants of the Dispersion Formula and Chemical Structure. Table 1 shows that the values of λ_0 are as follows (in units of 10^{-5} cm):

1) for saturated aliphatic hydrocarbons: methane 1.04, ethane 1.07, propane 1.10, hexane 1.17, heptane 1.14, octane 1.18, 2,2,4-trimethylpentane 1.24;

2) for hydrocarbons having one double bond: ethylene 1.45, propene 1.49, 1-hexene 1.45, 1-heptene 1.40, 1-octene 1.42, 2,2,4-trimethylpentene 1.49;

3) for hydrocarbons having two isolated double bonds: 1,5-hexadiene 1.57, dipentene-diprene mixture 1.57;

4) for hydrocarbons having two conjugated double bonds: isoprene 2.11;

5) for hydrocarbons having three conjugated double bonds: alloocimene 2.69.

These data clearly show the relation existing between the constant λ_0 and the chemical structure of the hydrocarbons.

Table 1 also gives the values of f:

1) for saturated aliphatic hydrocarbons: methane 1.27, ethane 1.94, propane 2.56, hexane 11, heptane 15, octane 13, 2,2,4-trimethylpentane 12;

2) for cycloalkanes: cyclopentane 7.6, methylcyclopentane 7.8;

3) for hydrocarbons having one double bond: ethylene 0.74, propene 0.90, 1-hexene 5.5, 1-heptene 7.3, 1-octene 7.9, 2,2,4-trimethylpentene 6.8.

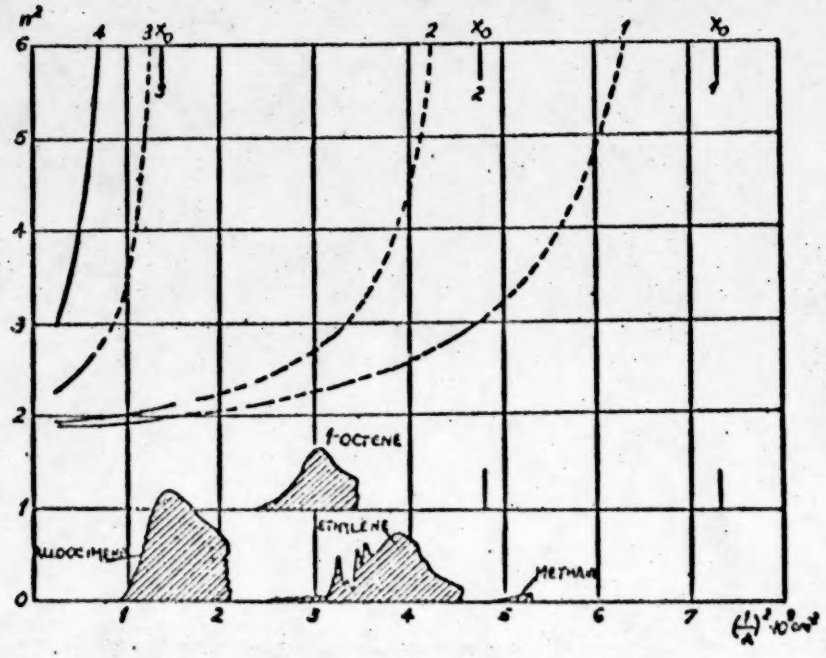

Fig. 8. Dispersion curves: 1) hexane; 2) hexene; 3) alloocimene; 4) anthracene crystal [11]. Values of ν_0^2 from the dispersion curves of the same substances are indicated by X_0 with the numbers 1, 2, 3, and 4. The continous lines are the measured sections of the dispersion curves. The broken lines are the extrapolated parts of the dispersion curves. The lower part of the diagram shows absorption curves for methane [9], ethylene and 1-octene [10], and alloocimene [12]

4) for hydrocarbons having two isolated double bonds: 1,5-hexadiene 4.7, dipentene-diprene mixture 6.5;

5) for hydrocarbons having two conjugated double bonds: isoprene 1.5;

6) for hydrocarbons having three conjugated double bonds: alloocimene 1.8.

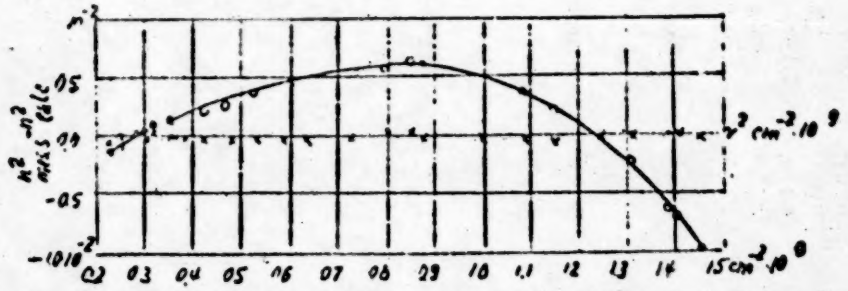

Fig. 9. Comparison with experiment of results for 1-octene obtained from formula (2) by the use of constants from Table 1 (the curve) and obtained from the same formula (2) by the use in it of the value of λ_0 from the paper [10] ($1.8 \cdot 10^{-5}$ cm)

All our values of $\underline{f}$ are collated in Fig. 7, which gives also the values of $\underline{f}$ for methane, ethane, propane, butane, and ethylene which we calculated by formula (2) from the experimental values of μ obtained by Friberg [8]. As will be seen, the values calculated from Friberg's data agree very well among themselves; the agreement of our own results is considerably worse, which is clearly to be associated with the fact that Friberg worked with shorter waves. In all cases, however, the effective strengths of the oscillators are colossally high, particularly when it is taken into account that for both D lines of sodium the oscillator strength is unity.

As stated above, Friberg could not find any relationship between the chemical structure and the constants which he obtained by calculations with a formula having four constants. We recalculated Friberg's results according to formula (2). The results of the calculation are given in Table 1. As will be seen, they fall into the same series of values of λ_0 and f as the values we have determined for other hydrocarbons. It will be obvious that the values of A and B, which depend on the density, cannot be the same for gases and liquids, and we therefore do not consider them.

Fig. 8 gives dispersion curves, extrapolated by formula (2) for hexane, 1-octene, alloocimene, and anthracene (C). This figure shows how far our extrapolation goes and gives an idea of the closeness of the agreement that we obtained.

6. Correlation of Dispersion Curves with Absorption Spectra. The absorption spectra of some hydrocarbons have recently been measured in the Schumann region [9, 10]. For methane, ethylene, and 1-octene absorption bands were detected at longer waves than we supposed in Table 1. In the paper [10], for example, an absorption curve for 1-octene is given for which $\lambda_{max} = 1.8 \cdot 10^{-5}$ cm; we assumed $\nu_0^2 = 3.25 \cdot 10^9$ cm^{-2} (instead of $4.97 \cdot 10^9$ cm^{-2}, as given in Table 1) and calculated an interpolation formula of type (3) with two constants; we obtained

$$n^2 = 1.6858 + \frac{9.141 \cdot 10^8}{3.25 \cdot 10^9 - \nu^2} \qquad (2^1)$$

The differences between the measured values of n^2 and those calculated from formula (2^1) are shown in Fig. 9, from which the magnitude of the discrepancies will be seen. It follows that our dispersion curves are determined by more intense absorption bands occurring in the ultraviolet region at shorter waves than the bands found experimentally in the cited investigations [9, 10].

It is necessary to continue the investigation of the dispersion curve into the shorter-wave region of the ultraviolet. As the absorption bands are approached, their effect on the dispersion curve will be more and more pronounced. If we take into account the component of the dispersion curve that is determined by the absorption bands discovered in the investigations [9] and [10], we should be able to fix the positions of the more distant ultraviolet bands with greater accuracy and, with the discovery of these, move further and further into the far ultraviolet and, extrapolating the dispersion curve, find still more new absorption bands.

SUMMARY

1. Dispersion curves were determined for hexane, lieptane, 1-octane, 2,2,4-trimethylpentane, cyclopentane, methylcyclopentane, 1,5-hexadiene, a mixture of dipentene and diprene isomers, isoprene, and alloocimene in the wavelength range 6500-2500 A.

2. For all of these hydrocarbons, the constants of a single-term Sellmeier formula were calculated. It was shown that there is a relationship between λ_0 and the number and positions of the double bonds present in the hydrocarbon. The dependence of f on the structure of the molecule is pointed out.

3. A method is proposed for the recording of refractive indices in the ultraviolet region of the spectrum.

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COMPARATIVE STUDY OF THE OXIDATION REACTIONS OF PECTIC SUBSTANCES, OF CELLULOSE, AND OF THE STRUCTURAL UNITS OF THESE SUBSTANCES

COMMUNICATION 2. OXIDATIVE DEGRADATION OF SODIUM POLYGALACTURONATE BY MEANS OF MOLECULAR OXYGEN, SODIUM METAPERIODATE, AND HYDROGEN PEROXIDE

O. P. Golova and N. S. Mayat

Pectic substances – natural high polymers having chain molecules – are to be found in association with cellulose in almost all plant tissues. It is known that pectic substances can be degraded in a homogeneous medium by various oxidizing agents (chlorine, bromine, periodic acid, hydrogen peroxide, potassium permanganate) with formation of substances of lower molecular weight [1]. However, this matter has not been investigated systematically.

We have studied the oxidative degradation of pectic substances in a homogeneous medium under the action of molecular oxygen, sodium metaperiodate, and hydrogen peroxide: the process was investigated quantitatively, some of the laws governing it were established, and the nature of the oxidative changes in the structural units was determined. As the simplest subject for investigation, we selected polygalacturonic acid, since this forms the skeleton of pectic substances, whatever their origin may be: we prepared it by alkaline hydrolysis of citreous pectin and purified it from accompanying substances (hexosans, pentosans, and carbohydrates containing aldehyde groups). As macromolecular polygalacturonic acid is of low solubility in water, its soluble sodium salt was used for investigation under homogeneous conditions (in aqueous solution).

In our quantitative study of the degradation of sodium polygalacturonate we employed methods based on the viscosity of its sols or solutions and on the determination of the functional groups (aldehyde and carboxyl groups) arising during the oxidation. In all cases the degradation was studied in alkaline solution (pH 12-13). For this reason, electro-viscous phenomena, characteristic of polygalacturonic acid solutions (a heteropolar colloid), were absent. Under these conditions, we were able to characterize the oxidative degradation of sodium polygalacturonate by rate constants calculated from the rate of change of the viscosity of the solution.

We studied the degradation of sodium polygalacturonate by molecular oxygen at various temperatures and for various concentrations of the reactants. The results enabled us to characterize the degradation reaction by rate constants and temperature coefficient.

Oxidative degradation by molecular oxygen (air) was studied at 20°, about 80°, about 90°, and 135°. The experiments at 20° showed that practically no degradation occurred during the period of time allowed (two hours), the rate constant for the reaction being zero (Table 1 and Fig. 1). Also, there were no changes in the contents of functional groups (Table 2).

When the temperature is raised to 80°, degradation begins to occur at an appreciable rate. With further rise in temperature the rate of degradation rises rapidly, as can be seen from the increase in the value of the rate constant (Table 1 and Fig. 2). At the same time there is an increase also in the number of functional groups (aldehyde and carboxyl groups) (Table 2). On the basis of these results we determined the temperature coefficient for the reaction (1.62).

The effect of the concentration of oxidant (molecular oxygen) on the degradation of sodium polygalacturonate was then studied at a given temperature (95°) (Table 3). Variation of the concentration of oxygen in the reaction medium was effected by variation of its concentration in the gas mixture passed through the solution, the rate of passage (5-6 ml/minute) and the duration of passage (two hours) being maintained constant.

The oxygen concentrations used were 100%, 20% (air), and 0.04% (argon containing oxygen). Oxidation was carried out also at an oxygen concentration that was very close to zero, this being attained by the introduction of an

TABLE 1

Rate Constant (k) for the Degradation of Sodium Polygalacturonate during Oxidation by Molecular Oxygen (Air) and Various Temperatures

Temperature (°C)	$k \cdot 10^3$	Temperature (°C)	$k \cdot 10^3$
20	0	92	7.27
82	4.46	135	47.60

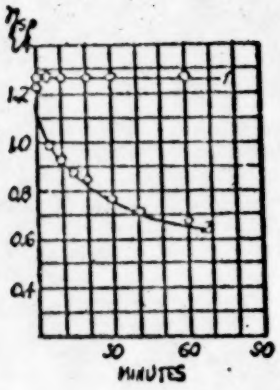

Fig. 1. Degradation of polygalacturonic acid during oxidation by sodium metaperiodate and atomspheric oxygen at 20°: 1 - oxidation by atmospheric oxygen; 2 - oxidation by $NaIO_4$.

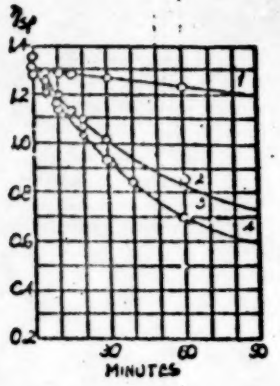

Fig. 3. Effect of the oxygen content of the gas mixture on the degradation of polygalacturonic acid during oxidation by molecular oxygen: 1 - 0%; 2 - 0.04%; 3 - 20%; 4 - 100% of oxygen.

inhibitor (glucose at concentrations of 10% and 20% by weight). The degradation rate constants for these conditions are given in Table 3 and Fig. 3.

The results in Table 3 show that, as would be be expected, change in the concentration of oxidant over a very wide range (100-0.04%) has little effect on the value of the rate constant, the change over this range being only from $10.53 \cdot 10^{-3}$ to $7.87 \cdot 10^{-3}$. On the other hand, reduction of the concentration of oxidant from 0.04% to

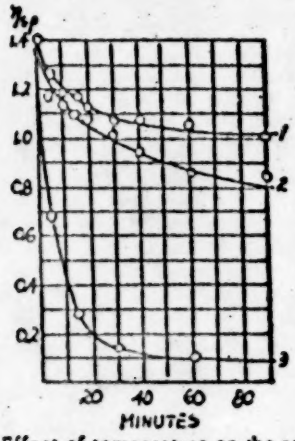

Fig. 2. Effect of temperature on the rate of degradation of polygalacturonic acid during oxidation by atmospheric oxygen: 1 - at 82°; 2 - at 92°; 3 - at 135°.

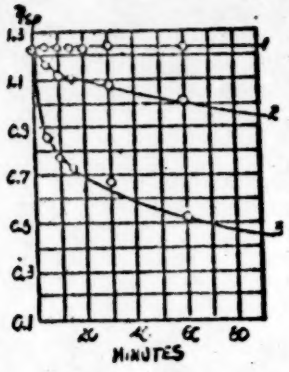

Fig. 4. Degradation of polygalacturonic acid during oxidation by hydrogen peroxide under various conditions: 1 - at 20°; 2 - in presence of a catalyst; 3 - at 95°.

almost zero by the introduction of 10% of inhibitor greatly retards oxidative degradation: the rate constant for the degradation reaction is reduced in the ratio of 9.2 : 1 (Table 3 and Fig. 3). Thus, at temperatures in the region of 100° the degradation of sodium polygalacturonate can be brought about by extremely small amounts of molecular oxygen, a result that is in full accord with Golova and Ivanov's results on the effect of very small amounts of oxygen on the oxidative degradation of cellulose in cuprammonium solution [2].

TABLE 2

Contents of Functional Aldehyde and Carboxyl Groups in Polygalacturonic Acid after Oxidation for 30 minutes

Oxidant and oxidation conditions	Number of CHO groups per 1000 repeating units	Number of COOH groups per 1000 repeating units
Atmospheric oxygen at 20°	5.6	811.2
Atmospheric oxygen at 95°	8.4	817.6
Atmospheric oxygen at 135°	21.6	–
Sodium metaperiodate at 20°	12.0	–
Hydrogen peroxide at 20°	6.4	804.8
Hydrogen peroxide at 95°	16.8	832.0
Hydrogen peroxide at 20° in presence of a catalyst	11.4	802.4
Unoxidized material	6.0	800.0

TABLE 3

Rate Constants for the Degradation of Sodium Polygalacturonate during Oxidation by Molecular Oxygen at 95°for Varying Concentrations of Oxygen in the Gas Phase.

Oxygen content of gas phase (%)	$k \cdot 10^3$
~100	10.53
~20	8.50
~0.04	7.87
~0	0.85

TABLE 4

Rate Constants for the Degradation of Sodium Polygalacturonate during Oxidation by Sodium Metaperiodate and Hydrogen Peroxide under Various Conditions.

Oxidant and conditions of oxidation	$k \cdot 10^3$
Sodium metaperiodate at 20°	16.20
Hydrogen peroxide at 20°	0
Hydrogen peroxide at 95°	10.84
Hydrogen peroxide at 20° in presence of a catalyst	4.60

Our results enabled us to make an approach to an explanation of the mechanism of the oxidative degradation. On the basis of these results it may be supposed that the primary cause of the degradation of sodium polygalacturonate in an alkaline medium at temperatures in the region of 100° is not the hydrolysis of the glucoside link under the influence of the carboxyl group standing at C-6, but the conversion of hydroxyls on C-1, C-2, and C-3 into other functional groups, with the result that the glucoside link is weakened and undergoes hydrolysis in an alkaline medium. It is known that such groups may be aldehyde and ketone groups, and also carbonic ester groupings [3, 4]. It is in fact found that practically no degradation of polygalacturonic acid is produced at 20° by molecular oxygen, this being associated with the absence of the formation of functional groups.

With increase in temperature the rate of degradation increases and there is an accompanying formation of new functional groups (aldehyde and carboxyl groups). This can be seen more clearly from the example of the degradation of polygalacturonic acid by sodium metaperiodate, for it is known that sodium metaperiodate breaks the bond between C-2 and C-3 in the structural units of cellulose and polygalacturonic acid with formation of two aldehyde groups [5].

The degradation of sodium polygalacturonate by sodium metaperiodate was studied in an alkaline medium at 20°. The concentration of oxidant was equivalent to 0.5 g/liter of active oxygen in the solution. The results – rate constant for the degradation reaction (Table 4 and Fig. 1) and aldehyde contents of the oxidation products (Table 2) – show that oxidation by sodium metaperiodate results in rapid degradation of polygalacturonic acid accompanied by rapid increase in the number of aldehyde groups.

These results confirm that the degradation of sodium polygalacturonate, not only by sodium metaperiodate but also by molecular oxygen, results from the oxidation of hydroxyls with formation of new functional groups (aldehyde groups) that reduce the stability of the glucoside link in an alkaline medium. It should be noted that the increase in the content of aldehyde groups during oxidation by molecular oxygen or sodium metaperiodate is considerably greater than the increase that could occur under these conditions as the result of the hydrolysis of the glucoside links of the polymer in an alkaline medium. The same is found in oxidation by hydrogen peroxide.

Unlike sodium metaperiodate, hydrogen peroxide, in oxidizing the hydroxyls at C-2 and C-3 of the structural unit of cellulose, yields not only aldehyde, but also ketone groups [4]. Like aldehyde groups, such ketone groups reduce the stability of the glucoside link in an alkaline medium and facilitate its rupture.

The degradation of sodium polygalacturonate by hydrogen peroxide was studied at 20° and 95°, and also at 20° in presence of a catalyst. The results (Tables 2 and 4, Fig. 4) show that at 20° the sodium salt is as stable to hydrogen peroxide as it is to molecular oxygen. Rise in temperature to 95° or introduction of a catalyst brings about degradation at a rate depending on the conditions.

EXPERIMENTAL

Preparation of Polygalacturonic Acid from the inner Skin (Albedo) of Citreous Fruits

1. Isolation of Pectin from Albedo. The albedo was removed from a fresh orange, ground, and extracted with water at 30° for 24 hours. The extract was filtered and poured into twice its volume of alcohol. The precipitated white mass of pectin was filtered off, pressed off, and dissolved in a little water. It was then reprecipitated with alcohol, filtered off, washed with alcohol and ether, and dried in the air.

2. Preparation of Polygalacturonic Acid by the Alkaline Hydrolysis of Pectin. The pectin (10 g) was dissolved with stirring in 1 liter of 0.1 N NaOH at room temperature. The temperature was raised slowly to 40°, and the solution was then filtered and poured slowly into excess of hydrochloric acid. The precipitated pectic acid was filtered off, washed with alcohol until the reaction for chloride was negative, washed further with ether, and dried in the air.

3. Purification of Polygalacturonic Acid from Reducing and Coloring Matters. The polygalacturonic acid was treated with an acid solution (pH 3-4) of sodium chlorite (0.1 N) for 20 hours at room temperature. The acid was then filtered off, washed with 60% alcohol until reaction for chloride was negative, washed further with ether, and dried to constant weight over phosphoric oxide in a vacuum desiccator. The polygalacturonic acid obtained in this way was found to contain 0.05% of aldehyde groups, 0.02% of methoxyl groups, and 20.04% of carboxyl groups. Further purification did not result in increase in carboxyl content.

Preparation of Solutions of Sodium Polygalacturonate in 0.05 N NaOH

In order to prepare 0.5% solutions of sodium polygalacturonate, an accurately weighed 0.450-g sample of polygalacturonic acid was dissolved in an equivalent amount of 0.1 N NaOH. The solution was filtered through a No. 2 glass filter and transferred to a 100-ml measuring flask; a further 50 ml of 0.1 N NaOH was added, and the solution was made up to the mark with water. Solutions of lower concentration (0.25% and 0.125%) were prepared by the same method, but the amounts of acid and alkali taken were correspondingly reduced.

Determination of the Viscosities of Solutions of Sodium Polygalacturonate in an Alkaline Medium

Ten milliliters of a solution of the salt prepared as indicated above was transferred to an Ostwald viscometer contained in a 20° thermostat. The solution was maintained at this temperature in the viscometer for 2-3 minutes, and the time of efflux of the solution was then determined. The determination was repeated three times. The time of efflux was determined in the same way for the solvent, i.e. 0.05 N NaOH. The specific viscosity was calculated by the formula $\eta_{sp} = (t - t_0)/t_0$, in which η_{sp} is the specific viscosity, t is the time of efflux of the solution seconds, and t_0 is the time of efflux of the solvent (seconds).

Degradation of Sodium Polygalacturonate during Oxidation by Molecular Oxygen, Sodium Metaperiodate, and Hydrogen Peroxide

Oxidation by Molecular Oxygen. The 0.5% solution of the sodium salt prepared as indicated above was poured into a Drechsel bottle. The bottle was placed in a thermostat at the required temperature and connected, on the one side through a small bottle containing the same solution to a gas meter and, on the other, to a Mariotte bottle. When the required temperature was attained in the solution, the heated gas was passed at 5-6 ml/minute. Oxidation was continued for three hours, the volume of gas passed during this period being about 1 liter.

After 5, 10, 15, 20, 30, 60, 120, and 180 minutes from the commencement of oxidation, passage of oxygen was interrupted and 10 ml of the solution was transferred by pipet to a bottle having a ground-in stopper. The solution was cooled rapidly and transferred to an Ostwald viscometer; its specific viscosity was then determined as described above. In this way oxidation with molecular oxygen was carried out at different concentrations in the gas mixture: ~100%, ~20% (air), 0.04%, and ~0%. In the oxidation with molecular oxygen (air) in presence of glucose, the concentration of the latter in the solution was 10% by weight; in other respects the experimental procedure remained the same.

Oxidation by Molecular Oxygen (Air) under Pressure. The 0.5% solution of sodium polygalacturonate prepared

as indicated above was introduced in 11-12-ml portions into 15-20-ml ampoules, which were sealed and placed in a thermostat at 135-140°. After 5, 10, 15, 20, 30, 40, 60, 120, and 180 minutes from the commencement of oxidation (the commencement was taken to be the moment at which a temperature of 135° was attained), ampoules were taken from the thermostat, rapidly cooled in ice water, and opened. The solution was transferred to an Ostwald viscometer, and its specific viscosity was determined.

Oxidation by Sodium Metaperiodate. Ten milliliters of a 0.5% solution of sodium polygalacturonate was transferred by pipet to a viscometer contained in a 20° thermostat, and the calculated amount of a saturated solution of sodium metaperiodate was added. The contents of the viscometer were mixed rapidly, and the time of mixing was taken to be the time of the commencement of oxidation. After 5, 10, 15, 20, 30, 60, 120, and 180 minutes from the commencement, the specific viscosity was determined. Parallel determinations were made on the solutions before oxidation, a volume of distilled water equal to the volume of metaperiodate introduced being added to 10 ml of the solution.

Oxidation by Hydrogen Peroxide. A 0.5% solution (100 ml) of sodium polygalacturonate was introduced into a round-bottomed flask fitted with reflux condenser, and the flask was placed in a thermostat at the required temperature. Oxidation was considered to begin when the maximum temperature was attained in the solution (92°). After 5, 10, 15, 20, 30, 40, 60, 120, and 180 minutes from the commencement of oxidation, 10 ml of solution was removed by pipet, cooled, and transferred to a viscometer.

Separation of Oxidized Preparations of Polygalacturonic Acid from Solutions of the Sodium Salts After being oxidized for 30 minutes, the solution of the sodium salt was cooled with ice water and poured into excess of 0.1 N HCl. The voluminous precipitate of polygalacturonic acid was filtered off, washed with hydrochloric acid, pressed off, and then allowed to stand overnight in 0.1 n HCl to complete demineralization. It was then filtered off, washed with 60% alcohol until reaction for chloride was negative, then washed with 96% alcohol and with ether, and dried over phosphoric oxide to constant weight.

SUMMARY

1. When molecular oxygen, sodium metaperiodate, and hydrogen peroxide react with sodium polygalacturonate, oxidative degradation may occur at a rate that depends both on the identity of the oxidant and on the oxidation conditions (temperature, concentration of oxidant, presence of catalyst).

2. The cause of the degradation of sodium polygalacturonate under these conditions is the formation of new functional groups, which brings about rupture of glucoside links in an alkaline medium. An essential condition for degradation is the use of oxidizing agents that act preferentially on the hydroxyls at C-2 and C-3.

3. The oxidation of C-2 and C-3 hydroxyls can be effected not only by the specific oxidant, sodium metaperiodate, but also by molecular oxygen and by hydrogen peroxide at temperatures in the region of 100°, and also by hydrogen peroxide in presence of a catalyst at room temperature.

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SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 13. GENERAL METHOD FOR THE SYNTHESIS OF VINYL SULFIDES

M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova

Few simple accessible methods have been reported for the preparation of unsaturated sulfur compounds which, on account of the presence of reactive double bonds in their molecules, could be used in the synthesis of various new substances. We now report a general method of the synthesis of one class of such substances – vinyl sulfides. The method is based on the vinylation of thiols as already applied by us for the preparation of ethyl vinyl sulfide [1, 2] and a series of alkoxyethyl vinyl sulfides [3]:

$$RSH + CH \equiv CH \xrightarrow[135\text{-}155^\circ]{5\%\ KOH} RSCH = CH_2 \qquad (1)$$

We showed [1, 2, 3] that a good yield of the vinyl sulfide can be obtained only in presence of an excess of acetylene, which, to a considerable extent, suppresses the secondary reaction in which a 1,2-bis (alkylthio) ethane is formed:

$$RSH + RSCH = CH_2 \rightarrow RSCH_2CH_2SR. \qquad (2)$$

In an attempt to extend the reaction conditions that we had established to reaction between acetylene and other thiols we discovered that, depending on the structure of the thiol, it was necessary to make considerable changes in such parameters of the process as temperature and catalyst concentration and also to introduce solvents and diluents. For example, at 135-150° in presence of caustic potash and excess of acetylene, 1-butane-, 1-propane-, 3-methyl-1-butane-, and α-toluene-thiols were completely resinified. This behavior is probably associated with the thermal instability of these compounds [4]. The use of solvents such as benzene, toluene, and ethanol and lowering of the vinylation temperature to 100-110° without introduction of solvent did not give the desired results. We then tried the use of water as a diluent, since it is known to reduce resinification considerably in the synthesis of aryl vinyl ethers [5]. We lowered the reaction temperature to 70-90° and diluted the reaction mixture (which contained 10 mole-% of KOH) with water; we were then able to synthesize butyl vinyl sulfide in about 30% yield. However, in this case the best results were obtained by the use as solvent of dioxane, which can dissolve considerable amounts of acetylene under pressure. This property of dioxane makes it easy to create a large excess of acetylene (2.5-3 moles per mole of thiol)* during the vinylation. Treatment of 1-butanethiol under these conditions (at 70-90°) yielded butyl vinyl sulfide in 70% yield. The actual yield of butyl vinyl sulfide was somewhat higher, since some losses evidently occurred as a result of the necessity of washing the reaction products with water to remove dioxane.

Under the same conditions other aliphatic vinyl sulfides were prepared in 65-75% yield, i.e. propyl vinyl sulfide, isopentyl vinyl sulfide, and the aralkyl sulfide benzyl vinyl sulfide. A somewhat lower yield was obtained in the vinylation of benzenethiol (50% in a dioxane medium and 70-72% in a butanol medium).

The method that we have proposed – which is based on the reaction of thiols with acetylene indiluted with inert gases and is a further development of Favorsky and Shostakovsky's reaction – permits us, therefore, to synthesize vinyl sulfides of any structure. In this respect the method differs essentially from the patented method of vinylating mercaptans with an acetylene-nitrogen mixture [7], which gives good yields only for aryl vinyl sulfides.

* This property of dioxane has already been applied by two of us in collaboration with Tsymbal for the preparation of the tetravinyl ether of methyl glucoside [6].

TABLE 1

Physical Properties of Vinyl Sulfides*

No.	R	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR		Yield (%)
					Found	Calculated	
1	C_2H_5	91.9-92.2 (760)	0.8767	1.4756	28.37	28.12	61.0
2	n-C_3H_7	43.5 (50)	0.8723	1.4734	32.89	32.86	60.0
3	n-C_4H_9	47.5-48.5 (24)	0.8698	1.4722	37.47	37.48	70.0
4	i-C_5H_{11}	53.5-54.5 (17)	0.8615	1.4704	42.21	42.09	65.0
5	$C_6H_5CH_2$	90-90.5(7)	1.0347	1.5794	48.28	47.73	76.2
6	C_6H_5	76.5 (4)	1.0417	1.5888	44.05	43.12	71.6

* For vinyl sulfides the literature gives: No. 4 b.p. 30-32° (4 mm); n_D^{20} 1.4715, d_4^{20} 0.8656 [8]; No. 5 b.p. 73° (3 mm) [7]; No. 6 b.p. 200-201°; n_D^{18} 1.5853 [9]; b.p. 76-78° (4 mm) [10].

TABLE 2

Comparison of the Boiling Points of alcohols ROH and thiols RSH with those of Vinyl Ethers $ROCH{=}CH_2$ and Vinyl Sulfides $RSCH{=}CH_2$ Synthesized from them

No.	R	B.p. (°C at 760 mm)		Δt (°C)	B.p. of thiol (°C at 760 mm)	B.p. of vinyl sulfide in °C (p in mm)	Δt (°C)
		of alcohol	of vinyl ether				
1	C_2H_5	78.0	36.0	−42.0	34.4-34.6	91.9-92.2 (760)	+57.5
2	n-C_3H_7	97.0	65.0	−32.0	67.4-67.6	43.5 (50)	~+50.0
3	n-C_4H_9	117.0	93.8	−23.2	98.6-99	144.0 (760)*	+45.0
4	i-C_5H_{11}	131.1-131.4	112.5-112.7	−18.6	120.1	54 (17)	~+40
5	C_6H_5	182.3-182.5	155-156	−27.3	166-169	200-201 (760)	+32
6	$C_6H_5CH_2$	205.3	183-184	−22.3	194-195	90-90.5 (7)	+30-40

* with decomposition

TABLE 3

Physical Properties of 1,2-Bis(alkylthio) - and 1,2-Bis(arylthio)-ethanes*

No.	$RSCH_2CH_2SR'$	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR	
					Found	Calculated
1	$C_3H_7SCH_2CH_2SC_3H_7$	91-92.5 (3)	1.5046	0.9565	55.27	55.08
2	$C_4H_9SCH_2CH_2SC_4H_9$	131-132 (6)	1.4967	0.9355	64.53	64.32
3	$C_4H_9SCH_2CH_2SC_2H_5$	98.5 (3.5)	1.5013	0.9539	55.08	55.08
4	$C_4H_9SCH_2CH_2SCH_2CH_2OC_4H_9$	155 (4)	1.4900	0.9600	75.42	75.20
5	$C_6H_5SCH_2CH_2SC_6H_5$	67.5 (m.p.)	–	–	–	–

* No. 1 and 2 were obtained by the vinylation of thiols, and No. 3, 4, and 5 were prepared by simple mixture of thiol and sulfide in the open. The literature gives: for No. 2 b.p. 129-130° (5 mm), d_{15}^{15} 0.3989; n_D^{20} 1.4962 [20]; and for No. 5 b.p. 69° [7].

Vinyl sulfides are volatile substances of unpleasant odor. They are insoluble in water, but tend to attract moisture, from which it is difficult to free them. Vinyl sulfides are best preserved in sealed ampoules from which air has been displaced by dry nitrogen, and these should be kept in the dark, since, under the action of light – particularly in the presence of oxygen – the vinyl sulfides tend to polymerize. Table 1 gives the physical properties of the vinyl sulfides that we have synthesized, including the previously described ethyl vinyl sulfide [1, 2].

It will be seen from Table 1 that for the aliphatic vinyl sulfides the exaltation of molecular refraction is not great – 0.1-0.25 on the average – which indicates that the interaction between the electrons of the double bond and of the sulfur atom is low*.

* In the calculation of molecular refraction, the value of the atomic refraction of sulfur found for diallyl sulfide (8.04) was used [11].

TABLE 4

Synthesis of Butyl Vinyl Sulfide

Expt. No.	Amount taken					Reaction conditions*		Yield of reaction products (%)	
				Of solvent					
	of 1-butanethiol (g)	of acetylene (moles per mole of thiol)	of KOH (mole-%)	Name of solvent	Amount (g)	Temperature (°C)	Duration of heating hours	Butyl vinyl sulfide	1,2-Bis(butylthio)ethane
1	7.0	1.6	8	–	–	150-160	1.5	–	–
2	7.0	1.6	8	Benzene	7.0	135-145	1.5	–	–
3	6.2	1.9	5	Ethanol	6.0	160-170	1.5	–	–
4	8.5	1.4	5	Toluene	15.0	155-165	2.0	–	–
5	8.0	1.2	10	–	–	100-110	1.5	–	–
6	8.0	1.2	10	Water	8.0	70-90	1.5	30.0	–
7	25.0	1.2	100	Water	55.0	70-90	3.0	30.0	14.0
8	30.0	2.4	20	Dioxane	45.0	70-90	1.0	62.0	9.0
9	106.5	3.1	20	Dioxane	180.0	70-90	1.0	70.0	6.5

*The capacities of the autoclaves used were as follows: Experiments 1-6, 150 ml; Experiments 7 and 8, 500 ml; and Experiment 9, 2500 ml. In Experiments 1, 3, 4, and 5 only resin was isolated, but in Experiment 2 some unchanged thiol was present, in addition to resin.

TABLE 5

Synthesis of Propyl, Isopentyl, Benzyl, and Phenyl Vinyl Sulfides $RSCH=CH_2$

R	Expt. No.	Amount taken					Reaction conditions*		Yield of reaction products (%)	
					Of solvent					
		of thiol (g)	of acetylene (moles per mole of thiol)	of KOH (mole-%)	Name of solvent	Amount (g)	Temperature (°C)	Duration of heating hours	Vinyl sulfide	1,2-Bis(alkylthio) ethane
C_3H_7	1	6.0	1.8	10	–	–	135-150	1.0	–	–
	2	20.0	2.5	20	Dioxane	35	70-90	1.0	60.0	8.5
i-C_5H_{11}	1	8.0	1.8	10	–	–	140-150	1.0	–	–
	2	27.0	2.5	20	Dioxane	45	70-90	1.0	65	–
$C_6H_5CH_2$	1	8.5	1.6	5	–	–	150-170	1.5	–	–
	2	8.0	2.6	20	Dioxane	15	70-90	1.0	76	–
C_6H_5	1	10.0	1.4	5	–	–	160-180	1.5	36.6	–
	2	30.0	1.4	5	–	–	160-180	1.5	40.0	–
	3	22.0	1.5	10	Water	5	160-180	2.5	40.7	–
	4	30.0	1.4	10	Butanol	30	145-160	3.0	71.6	–
	5	30.0	2.0	20	Dioxane	45	90-110	1.0	50.0	–

For the quantitative analysis of the vinyl sulfides and the determination of their purity we used the cleavage reaction with excess of alcoholic mercuric chloride, already described in various papers [2, 3]:

$$RSCH=CH_2 + HgCl_2 + 2\,C_2H_5OH \rightarrow RSHgCl + HCl + CH_3CH(OC_2H_5)_2 \qquad (3)$$

In Table 2 comparisons are made between the boiling points of thiols [15-18] and the vinyl sulfides synthesized from them on the one hand and the boiling points of alcohols and the corresponding vinyl ethers on the other [12-14]. Vinyl ethers boil considerably lower than the original alcohols, since the boiling points of the latter are abnormally high as a result of association and do not correspond to their molecular weights. It is known that association between sulfur atoms by hydrogen bonding is not possible, so that in the series of thiols and sulfides the normal correspondence between boiling point and molecular weight is to be observed.

As already stated, the formation of vinyl sulfides is complicated by the secondary reaction in which 1,2-bis (alkylthio) ethanes are formed. These substances can readily be obtained as sole reaction product, and they may be prepared by direct reaction between thiols and the vinly sulfides in the air. This confirms the tendency of vinyl sulfides to undergo free-radical reactions which we have pointed out previously. Under the same conditions vinyl ethers give a mixture of addition products formed in accordance with and contrary to Markovnikov's rule [19]. In Table 3 we give the physical properties of the 1,2-bis (alkylthio)- and 1,2-bis (arylthio)-ethanes that we have synthesized.

EXPERIMENTAL

I. Synthesis of Vinyl Sulfides

The vinyl sulfides were synthesized in rotating autoclaves provided with heaters. The thiols were freshly distilled. The dioxane that was used in some of the experiments was purified by Hess and Frahm's method [21] and gave a negative reaction with pure mercury for the presence of the peroxide.

a) Synthesis of Butyl Vinyl Sulfide. The different variants tried for the synthesis of butyl vinyl sulfide are indicated in Table 4. One of the experiments is described by way of example.

Experiment 9. A mixture of 106.5 g of 1-butanethiol, 180.0 g of dioxane, and 13.2 g of KOH (20 mole-%) was prepared in an autoclave. The reaction mixture was completely saturated with acetylene in the cold, for which purpose it was passed into the autoclave in three doses, each followed by agitation for 10-15 minutes•. In this way, for each mole of thiol 3.1 moles of acetylene was introduced, of which 1.5 moles was in the gas phase and 1.6 moles in the dissolved condition. The temperature was maintained at 70-90° for one hour, and the maximum pressure attained was 30 atm. Ether (250 ml) was added to the reaction mixture, and the ether extract was washed with water (4-5 300-ml portions). The ether extract was dried over sodium sulfate (it is necessary to dry it for at least one day).

Ether was removed, and vacuum distillation then yielded the following fractions:

Fraction I, b.p. 35-50 (20 mm); 4.0 g; n_D^{20} 1.4705

Fraction II b.p. 50.5-51.5(20 mm); 96.0 g; n_D^{20} 1.4720

Fraction III B.p. 60-137 (6 mm); 1.5g; n_D^{20} 1.4850

Fraction IV B.p. 137-140 (6 mm) 8.5g; n_D^{20} 1.4965

Resinous residue 0.5 g

After refractionation, butyl vinyl sulfide (Fraction II) had b.p. 47.5-48.5° (21 mm); n_D^{20} 1.4722; d_4^{20} 0.8698; Calculated MR 37.48; Found MR 37.47.

Found %: C 62.10; 61.77; H 10.53; 10.52; S 27.64; 27.68

$C_6H_{12}S$. Calculated %: C 62.00; H 10.41; S 27.59

The content of butyl vinyl sulfide, determined by the mercuric chloride method [2,3], was 98.3 - 99.1%.

Fraction IV was 1.2-bis (butylthio) ethane, obtained in 7.5% yield; its constants were close to those given in the literature [20] (see Tabel 3).

Found % C 58.25; 58.29; H 10.79; 10.81; S 30.96; 31.12

$C_{10}H_{22}S_2$. Calculated % C 58.19; H 10.79; S 31.07

•In order to obtain the necessary excess of acetylene it is essential to use cylinders containing acetylene at not less than 15 atm (better, 17-18 atm).

TABLE 6

Analytical Results

Formula of substance	Combustion analysis [24]						Analysis by the mercuric chloride method [2, 3] %
	Found in %			Calculated in %			
	C	H	S	C	H	S	
$CH_2=CHSC_3H_7$	–	–	31.42,30	–	–	31.37	99.4-99.5
$C_3H_7SCH_2CH_2SC_3H_7$	54.18	9.98	35.70	53.87	10.17	35.95	–
	54.00	9.88	35.76				
$CH_2=CHSC_5H_{11}$(-i)	–	–	–	–	–	–	99.4-99.5
$CH_2=CHSCH_2C_6H_5$	71.92	6.72	21.38	71.95	6.71	21.34	97.2-97.9
	72.03	6.77	21.31				
$CH_2=CHSC_6H_5$	70.74	5.96	23.53	70.53	5.92	23.54	99.5-100
	70.78	6.01	23.28				

TABLE 7

Synthesis of 1,2-Bis(alkylthio)- and 1,2-Bis(arylthio)-ethanes

Expt. No.	Amount of vinyl sulfide taken		Amount of thiol taken		Yield of bis-ethanes (%)	Analytical results					
						Found in %			Calculated in %		
	Formula	Amount (g)	Formula	Amount (g)		C	H	S	C	H	S
1	$CH_2=CHSC_4H_9$	5.8	C_2H_5SH	4.5	100.0	53.88	10.27	35.89	53.87	10.17	35.96
						54.17	10.04	35.95			
2	$CH_2=CHSC_4H_9$	5.8	$CH_2OC_4H_9$• | CH_2SH	10.0	90.0	57.56	10.46	24.41	57.55	10.46	25.60
						57.75	10.37	25.70			
3	$CH_2=CHSC_6H_5$••	0.8	C_6H_5SH	1.0	100.0	–	–	–	–	–	–

• 2-Butoxyethanethiol was synthesized by the action of hydrogen sulfide on butyl vinyl ether [25].

•• The reaction product was not analyzed since its melting point was identical with that given in the literature (see Table 3).

This substance is 1,2-bis (butylthio) ethane, not 1,1-bis(butylthio)-ethane, for it does not give a pink color when an excess of alcoholic mercuric chloride is added in presence of Methyl orange [19].

In Experiment 7 (see Table 4), in which the 1-butanethiol to be vinylated was completely converted into mercaptide, not only butyl vinyl sulfide and 1,2-bis (butylthio) ethane were isolated, but also dibutyl sulfide, b.p. 54° (4 mm) and n_D^{20} 1.4548, was obtained in 12.5% yield. The salt formed by dibutyl sulfide with mercuric chloride melted at 111-112°. The literature gives $(C_4H_9)_2S$, b.p. 182° [22] and $(C_4H_9)_2S \cdot 2HgCl_2$, m.p. 111-112° [23].

b) The Conditions for the Synthesis of Other Vinyl Sulfides are summarized in Table 5; their physical properties are given in Table 1, and analytical data are given in Table 6.

Propyl and butyl vinyl sulfides have not been described in the literature. Isopentyl vinyl sulfide was prepared by Khomenko [8] in 45% yield [together with diisopentyl sulfide and 1,2-bis (isopentylthio)-ethane] by the action of acetylene on an aqueous solution of 3-methyl-1-butanethiol. The preparation of benzyl vinyl sulfide (without indication of the yield) and of phenyl vinyl sulfide (in 90% yield) by the action of an acetylene-nitrogen mixture on thiols is described in German patents [7]. Phenyl vinyl sulfide has been prepared also by the decomposition of dimethylphenyl (2-phenylthioethyl)- ammonium iodide [9] and by the pyrolysis of 1,2-bis (phenylthio) ethane [10].

II. Synthesis of 1,2-Bis (alkylthio)- and 1,2-Bis (arylthio)-ethanes

1,2-Bis (alkylthio)- and 1,2-bis (arylthio)-ethanes were prepared by mixing the corresponding thiols and sulfides in the open. After 5-10 minutes the mixture began to grow warm. When the thiol had a low boiling point, the temperature of the mixture was maintained at not above 20-25° by the aid of ice water. When high-boiling thiols

were used, the mixture was not cooled and the temperature rose to 70-80°. On the next day the reaction mixture was fractionated (Experiments 1 and 2). None of the synthesized substances gave an acid reaction to Methyl orange after addition of excess of alcoholic mercuric chloride, i.e., they were free from the isomeric mercaptals. The physical constants of these bis (alkylthio)- and bis (arylthio)-ethanes are given in Table 3, and the experimental conditions and analytical results are given in Table 7.

SUMMARY

1. A general method based on the Favorsky-Shostakovsky reaction was developed for the synthesis of vinyl sulfides of various structures. The essence of the method is reaction between thiols and excess of acetylene, undiluted by inert gas, in presence of caustic potash.

2. It was shown that, even under optimum vinylation conditions, a secondary process occurs with formation of bis (alkylthio)- and bis (arylthio)-ethanes. The latter substances can be prepared in theoretical yield by simply mixing vinyl sulfides with thiols in the open. This reaction indicates the great tendency of vinyl sulfides to undergo free-radical transformations.

3. It was shown that the cleavage of vinyl sulfides with excess of alcoholic mercuric chloride is quantitative and can be used for the titration of all vinyl sulfides.

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SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 7. VINYL ETHER OF 2-DIPHENYLAMINOETHANOL

M. F. Shostakovsky and I. A. Chekulaeva

Study of the properties of some vinyl ethers of ethanolamines has shown that the vinyl ethers of monoethanolamine $CH_2=CHOCH_2CH_2NH_2$ (I) and diethanolamine $(CH_2=CHOCH_2CH_2)_2NH$ (II) and $CH_2=CHOCH_2CH_2NHCH_2CH_2OH$ (III) are distinguished by chemical inertness in reactions characteristic for alkyl vinyl ethers, which occur in presence of ionogenic catalysts [1, 2]. This behavior is associated with the presence in their molecules of nitrogen and oxygen, which are capable of forming onium compounds, and with the presence also of a hydrogen bond of the type –N–H···O– [3].

The effect of a hydrogen bond is excluded in those vinyl ethers of ethanolamines which contain a tertiary amino group. It is in fact found that the vinyl ether of 2-diethylaminoethanol $CH_2=CHOCH_2CH_2N(C_2H_5)_2$ (IV), unlike the vinyl ethers (I), (II), and (III), reacts with alcohols. The effect of the presence of a nitrogen capable of forming onium compounds is still felt, however, and for the vinyl ether of 2-diethylaminoethanol acetal formation occurs under more severe conditions and in lower yield than for unsubstituted alkyl vinyl ethers. No polymerization at all will occur in presence of ionic catalysts [1].

In order to weaken the effect of the basic properties of the amino group, a phenyl radical may be introduced into it. The presence of only one phenyl radical already raises the reactivity of the vinyl ether. Thus, the vinyl ether of 2-anilinoethanol $CH_2=CHOCH_2CH_2NHC_6H_5$ (V), unlike the ethers (I), (II), (III), and (IV), readily undergoes several reactions in presence of traces of concentrated hydrochloric acid [4]. In view of these considerations it was of interest to determine the effect of the introduction of two phenyl radicals in the amino group of the vinyl ether of 2-aminoethanol. The present paper is devoted to the synthesis of the vinyl ether of 2-diphenylaminoethanol and the investigation of its properties. The ether was prepared by the vinylation of the corresponding amino alcohol:

$$(C_6H_5)_2NCH_2CH_2OH + HC\equiv CH \rightarrow (C_6H_5)_2NCH_2CH_2OCH=CH_2 \qquad \text{(VI)}$$

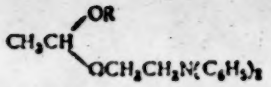
Investigation of the vinylation reaction showed that reaction between 2-diphenylaminoethanol and acetylene gives a good yield of the vinyl ether (65-75%), both in presence of caustic potash and in presence of the potassium derivative of the amino alcohol, as catalyst. In a study of the chemical properties of the resulting vinyl ether it was shown that it is hydrolyzed by 2% sulfuric acid with formation of acetaldehyde and the corresponding amino alcohol. Hydolysis is slow at 20°. Heating and vigorous agitation accelerate the reaction, but when heat is applied hydrolysis is accompanied by side reactions. Hydrogenation of the vinyl ether of 2-diphenylaminoethanol over Raney nickel resulted in the synthesis of the corresponding ethyl ether:

$$CH_3CH_2OCH_2CH_2N(C_6H_5)_2$$

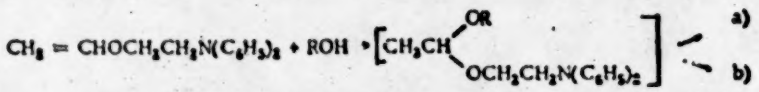
In a study of the addition of alcohols to the vinyl ether (VI), the alcohols taken as examples were methanol, butyl alcohol, and 2-diphenylaminoethanol. It was found that, unlike other vinyl ethers of ethanolamines studies (I-V) [1, 2, 4], the ether (VI) readily formed acetals in good yield (60-65%). In this way acetaldehyde bis 2-diphenylaminoethyl) acetal was prepared:

$$(C_6H_5)_2NCH_2CH_2OCH=CH_2 + HOCH_2CH_2N(C_6H_5)_2 \rightarrow CH_3CH\begin{matrix}OCH_2CH_2N(C_6H_5)_2\\ OCH_2CH_2N(C_6H_5)_2\end{matrix} \qquad \text{(VII)}$$

We did not succeed in preparing acetals of the following structure:



(R is CH_3 or C_4H_9) in a pure state, since on vacuum distillation (3 mm) they decomposed into alkyl vinyl ether (VIII) and 2-diphenylaminoethanol (IX). The presence of these two substances among the reaction products together with the isolated dialkyl acetal (X) and the bis(2-diphenylaminoethyl) acetal (XI) proves that these mixed acetals are formed. In the given case the reaction evidently proceeds as follows:



a) → $CH_3CH(OR)_2$ + $CH_3CH[OCH_2CH_2N(C_6H_5)_2]_2$
(X) (XI)

b) → $CH_2=CHOR$ + $HOCH_2CH_2N(C_6H_5)_2$
(VIII) (IX)

The polymerization of the vinyl ether of 2-diphenylaminoethanol was carried out in order to estimate its tendency to undergo this change. We succeeded in effecting polymerization both in the presence of ionic catalysts (concentrated hydrochloric acid and ferric chloride), and also in the presence of free-radical catalysts (2,2'-azobis[2-methylpropionitrile]). Under our conditions, however, the yield of polymer and the degree of polymerization were low. Products close in molecular weight to the dimer were obtained.

The behavior in the reactions of acetal formation and polymerization indicate the vinyl ether of 2-diphenylaminoethanol is more reactive not only than the vinyl ethers (I), (II), and (III), but also than the vinyl ether of 2-diethylaminoethanol (IV). Hence, the introduction of two phenyl radicals into the amino group not only excludes the effect of the hydrogen bond on the reactivity of vinyl ethers of ethanolamines, but also weakens the effect of the basic properties of the amino group to a considerable extent.

EXPERIMENTAL

1. Synthesis of the Vinyl Ether of 2-Diphenylaminoethanol*

2-Diphenylaminoethanol was prepared by reaction between diphenylamine and ethylene oxide in an autoclave at 220-240°. The yield was 60-65%. This amino alcohol is a very thick yellow liquid, which crystallizes after long standing. It has the following constants: b.p. 183-186° (5 mm); n_D^{20} 1.6210; d_4^{20} 1.121; MR 66.93; calculated for $C_{14}H_{15}ON$ MR 65.11; the literature [5] gives b.p. 169-171° (9-10 mm); d_4^{20} 1.116; n_D^{20} 1.629.

The vinylation of 2-diphenylaminoethanol was carried out in an autoclave in benzene or dioxane medium at 170-180° in presence of caustic potash or the potassium derivative of 2-diphenylaminoethanol as catalyst. The last compound was prepared by stirring and warming the amino alcohol (excess, 100-105° in flask, adding potassium (gradually, in the form of very small pieces). The results of the vinylation are given in Table 1.

Example. A mixture of 73.0 g of the amino alcohol, 8 g of its potassium derivative, and 200 ml of benzene was prepared in a two-liter autoclave, and acetylene at 14-16 atm was passed in. The amount of acetylene necessary for complete vinylation was absorbed in three hours at 180°. The reaction product was a thick dark-colored liquid, which was vacuum-fractionated. After removal of benzene, the following fractions were collected:

Fraction I, B.p. 100-158° (5 mm):	6.1 g
Fraction II, B.p. 158-165° (5 mm):	61.5 g
Resin	18.2 g

Fractions I and II were treated with sodium to remove traces of alcohol and were then distilled. The product, amounting to 61.5 g (74.5%), was the vinyl ether of 2-diphenylaminoethanol, a thick colorless liquid that rapidly yellowed in the air: b.p. 158-159° (3 mm); n_D^{20} 1.5980; d_4^{20} 1.0696, MR 76.34; Calculated for $C_{16}H_{17}ON$ MR 74.00.

The difference between the determined and calculated molecular refractions of the vinyl ether of 2-diphenylaminoethanol, and also of its derivatives, is probably to be explained by the presence of phenyl radicals in its molecule.

* Laboratory assistant V. A. Zabavina took part in conducting the experiments.

Found %: C 80.08; 79.90; H 7.02; 7.13; N 5.79; 5.84

$C_{18}H_{17}ON$. Calculated %: C 80.30; H 7.16 N 5.85

The literature [6] gives b.p. 150-160° (3 mm).

TABLE 1

Expt. No.	Catalyst (taken in the amount of 10% on the weight of amino alcohol)	Solvent	Duration of reaction hours	Yield of vinyl ether (%)	Amount of resin (% on weight of amino alcohol)
1	Potassium derivative	Benzene	5	75.5	28.4
2	Potassium derivative	Benzene	3	74.5	25.0
3	Potassium derivative	Dioxane	5.5	81.5	20.3
4	Caustic potash	Benzene	5	52.3	99.4
5	Caustic potash	Benzene	2.5	66.0	57.5
6	Caustic potash	Benzene	0.5	66.5	58.5

II. Hydrolysis of the Vinyl Ether of 2-Diphenylaminoethanol

The vinyl ether was hydrolyzed at 95° with 2% H_2SO_4. The hydrolysis was carried out in a three-necked flask fitted with mercury-sealed stirrer, thermometer, reflux condenser, and tube for the passage of gas. A mixture of 9.1 g of the vinyl ether and 100 ml of 2% H_2SO_4 was prepared in the flask. The acetaldehyde formed in the hydrolysis was removed by a stream of nitrogen and trapped by water in Tishchenko bottles. The acetaldehyde contents of the aqueous solutions were determined by the bisulfite method [7]. The reaction products were separated from the aqueous layer in the form of a solution in ether, and the ether solution was dried with potassium carbonate and distilled. The products were 6.6 g of 2-diphenylaminoethanol, 1.0 of acetaldehyde, and 1.3 g of a substance of molecular weight 398, which was not investigated further.

III. Hydrogenation of the Vinyl Ether of 2-Diphenylaminoethanol

The hydrogenation was carried out over Raney nickel (5% on the weight of the ether) at 100° in an autoclave. The reaction product was filtered from the catalyst, treated with sodium, and distilled. The ethyl ether of 2-diphenylaminoethanol was obtained as a colorless liquid, b.p. 158-159° (4mm); $n_D^{20.5}$ 1.5920; d_4^{20} 1.0600; MR 77.02; Calculated for $C_{16}H_{19}ON$ MR 74.47

Found %: C 79.96; 79.85; H 7.67; 7.45; N 5.91, 5.79

$C_{16}H_{19}ON$. Calculated %: C 79.63; H 7.94 N 5.80

IV. Synthesis of Acetaldehyde Bis (2-diphenylaminoethyl) Acetal (VII)

The acetal was prepared in a three-necked flask fitted with stirrer and thermometer. One drop of concentrated hydrochloric acid was added to a mixture of 8.7 g (0.036 mole) of the vinyl ether of 2-diphenylaminoethanol and 7.2 g (0.034 mole) of 2-diphenlaminoethanol (n_D^{20} 1.6220). There was a spontaneous rise of temperature, the maximum rise being 35°. Stirring was continued for four hours. The very viscous, dark-brown reaction product was vacuum-distilled, and 15.1 g of it gielded:

Fraction I, B.p. 165-280° (4 mm); 4.3 g

Fraction II, B.p. 281-288° (3.5 mm); 9.6 g

Resin 1.0 g

Redistillation of Fraction II yielded 9.5 g (62.5%) of the required acetal, a very thick, dark-yellow liquid, b.p. 282-284° (4 mm), n_D^{20} 1.6185, d_4^{20} 1.1175; MR 141.9; Calculated for $C_{36}H_{42}O_2N_2$ MR 137.5

Found %: C 79.33; 79.19; H 7.21; 7.25; N 5.95; 6.06

$C_{36}H_{42}O_2N_2$. Calculated %: C 79.61; H 7.13; N 6.19

V. Reaction of the Vinyl Ether of 2-Diphenylaminoethanol with Butyl Alcohol

The procedure described in Section IV was followed. Reaction was between 14.0 g (0.058 mole) of the vinyl ether and 4.4 g (0.059 mole) of butanol (b.p. 115-117°; n_D^{15} 1.3990). The maximum rise in temperature was 38°. Vacuum fractionation of the products yielded 2.1 of the dibutyl acetal (b.p. 184-185°; n_D^{15} 1.4110), 5.5 g of the bis (2-diphenylaminoethyl) acetal [b.p. 275-280° (2-3 mm); $n_D^{15.5}$ 1.6187 (see preceding experiment)], and 10.1 g of a product that distilled with decomposition at 175-187° (3 mm). From the decomposition products, butyl vinyl ether (b.p. 92-94°; n_D^{18} 1.4035) and 2-diphenylaminoethanol [b.p. 180-183° (4 mm); n_D^{19} 1.6210] were isolated.

VI. Reaction of the Vinyl Ether of 2-Diphenylaminoethanol with Methanol

The reaction conditions were similar to those of the synthesis of the bis (2-diphenylaminoethyl) acetal (Section IV). A mixture of 15.9 g (0.066 mole) of the vinyl ether and 4.7 g (0.145 mole) of purified methanol (b.p. 65°; n_D^{19} 1.3312) was prepared in the flask. The maximum rise of temperature after the addition of one drop of concentrated hydrochloric acid was 53°. Vacuum distillation of 18.7 g of the reaction product yielded 1.8 g of the dimethyl acetal (b.p. 63-64°, n_D^{19} 1.3762); 9.2 g of the bis (2-diphenylaminoethyl) acetal [b.p. 275-277° (2-3 mm); n_D^{21} 1.6187], and 4.9 g of a product that distilled with decomposition at 170-178° (4 mm). 2-Diphenylaminoethanol was isolated from the decomposition products ($n_D^{15.5}$ 1.6235).

VII. Polymerization of the Vinyl Ether of 2-Diphenylaminoethanol

a) Polymerization in presence of Ferric Chloride and of Concentrated Hydrochloric Acid. Ferric chloride was used as a 5% solution in butyl alcohol. The polymerization was carried out in a three-necked flask fitter with thermometer and reflux condenser. The vinyl ether 23 g was brought to the boil under reduced pressure (163-164° at 3.5-4 mm), and one drop of catalyst was added through a capillary. The ether was maintained at the boiling point for four hours. The thick dark-bordeaux product was dissolved in acetone, and the polymer was precipitated from the acetone solution with methanol. It was then washed repeatedly with methanol and dried under reduced pressure (3-5 mm). The yield and characteristics of the polymer are given in Table 2. Vacuum distillation of the acetone-methanol solution yielded the original vinyl ether and a viscous dark-colored product (22-23% yield) having a molecular weight of 448-617. Elementary analysis indicated that this substance was a polymer of the vinyl ether of 2-diphenylaminoethanol, formed as a result of the further heating during distillation.

Found %: C 79.72, 79.85; H 7.10; 7.09; N 6.17; 6.08

b) Polymerization in presence of 2,2'-Azobis [2-methylpropionitrile]. The vinyl ether (15.7 g) was heated with the catalyst (2% on the weight of the ether) in a sealed glass tube at 60° for 100 hours continuously. The treatment of the reaction product was as in the preceding experiments (Section VII, a). A thick dark-yellow polymer molecular weight 475, was obtained in a yield of 0.4 g.

Found %: C 79.86; 79.75; H 7.28; 7.18; N 6.44; 6.42

TABLE 2

Expt. No.	Catalyst	Yield of polymer (%)	Amount of unchanged vinyl ether (%)	Molecular weight of polymer (determined cryoscopically in benzene)	Elementary analysis		
					C	H	N
1	Concentrated hydrochloric acid	31.2	38.6	420-460	80.18 80.30	7.40 7.20	5.84 6.23
2	Ferric chloride	29.8	43.0	626	79.86 79.97	7.10 7.11	6.36 6.40

Vacuum distillation of the acetone-methanol solution yielded 12.5 g of the original vinyl ether, 0.25 g of a sticky yellow solid (molecular weight 369), and 1.0 g of a thick resinous residue.

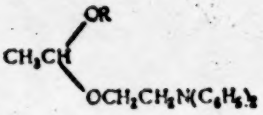
SUMMARY

1. The vinylation of 2-diphenylaminoethanol was studied.

2. The vinyl and ethyl ethers of 2-diphenylaminoethanol were prepared and characterized.

3. It was found that the vinyl ether of 2-diphenylaminoethanol, unlike other vinyl ethers of ethanolamines, reacts with alcohols under the conditions normally required by alkyl vinyl ethers and undergoes polymerization in presence of ferric chloride and of concentrated hydrochloric acid.

4. Acetaldehyde bis (2-diphenylaminoethyl) acetal was prepared.

5. It was shown that the acetals  in which R = CH_3 or C_4H_9, are unstable and decompose when distilled with formation of the alkyl vinyl ether and 2-diphenylaminoethanol.

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REACTIONS OF UNSATURATED AND MACROMOLECULAR COMPOUNDS

COMMUNICATION 6. COPOLYMERIZATION OF VINYLCAPROLACTAM WITH METHYL METHACRYLATE IN PRESENCE OF BENZOYL PEROXIDE AND OF 2,2'-AZOBIS [2-METHYLPROPIONITRILE]

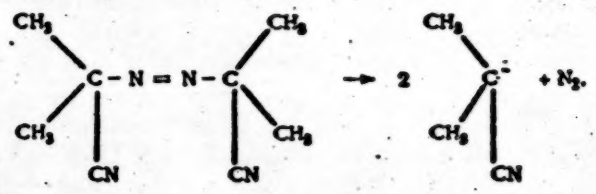
M. F. Shostakovsky, F. P. Sidelkovskaya, and A. M. Khomutov

It is known that polymers of vinylcaprolactam (2-oxo-1-vinylhexamethylenimine) are hydrophilic [1] and that polymers of methyl methacrylate are hydrophobic; it was of interest, therefore, to study the copolymerization of these monomers and to determine the effect of the nature of the monomers on the properties of the polymeric products formed.

There is very little information in the literature on the participation of vinylcaprolactam in copolymerization reactions. A patent [2] refers in a general way to the copolymerization of vinyl lactams, including vinylcaprolactam, with vinyl laurate and other vinyl esters of higher fatty acids (having not less than eight carbon atoms); the initiator used was 2,2'-azobis [2-methylpropionitrile].

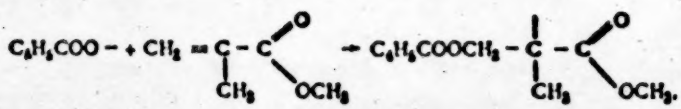
In the present investigation we studied the copolymerization of vinylcaprolactam with methyl methacrylate in presence of benzoyl peroxide and of 2,2'-azobis [2-methylpropionitrile], which initiate reactions proceeding by a free-radical mechanism. We have previously pointed out [3] that the activity of a monomer in a polymerization process varies according to the mechanism by which the reaction proceeds. It should be noted also that for a given mechanism the activity varies according to the character of the initiator. For example, initiation by benzoyl peroxide [4] and by the azo nitrile [5] results from the decomposition of these substances into radicals (Equations 1 and 2), so that in both cases the process proceeds by a free-radical mechanism:

$$(C_6H_5CO)_2O_2 \rightarrow 2C_6H_5COO- \quad (1)$$



(2)

However, the effects of these initiators in activating our monomers are different: it was found that benzoyl peroxide has very little tendency to bring about the polymerization of vinylcaprolactam, but promotes vigorous polymerization in methyl methacrylate; on the other hand the azo nitrile is very active in polymerizing both of these monomers. In spite of the fact that vinylcaprolactam does not polymerize to any appreciable extent in presence of benzoyl peroxide, it readily participates in copolymerization with methyl methacrylate in presence of this initiator. We observed a similar phenomenon previously in the copolymerization of methacrylic acid and vinyl ethers [6]. In the present case the process may be represented by the following equations:



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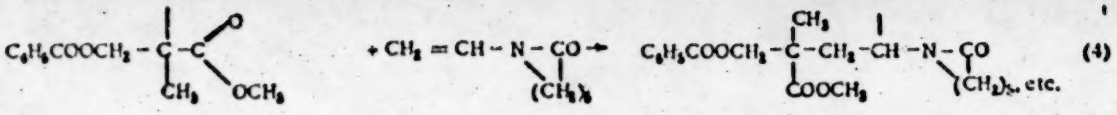

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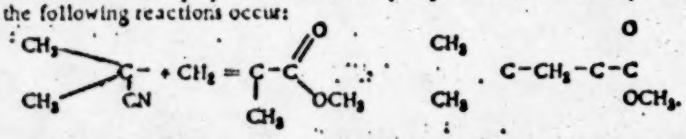
It is evident that in the copolymerization of vinylcaprolactam with methyl metacrylate in presence of the azo nitrile, the following reactions occur:



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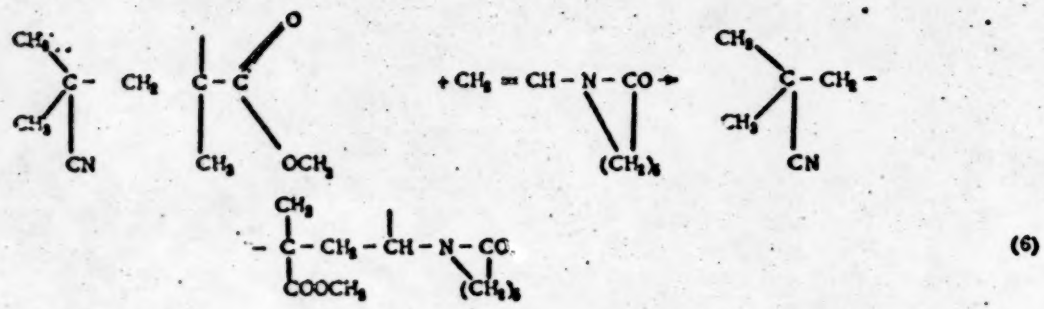


(6)

In our experiments on the copolymerization of vinylcaprolactam and methyl methacrylate, the reactants were taken in various proportions, and the results enabled us to establish the character of the process and the main laws governing its course. In Tables 1 and 2 we give the yields and compositions of the polymeric products obtained.

It will be seen from Table 1 that, when copolymerization occurs in presence of benzoyl peroxide, increase in the proportion of vinylcaprolactam in the original mixture of monomers results in a reduced yield of copolymer, but its content of vinylcaprolactam units increases. As the proportion of vinylcaprolactam increases, the viscosity of the copolymer increases a little at first, but then diminishes. The presence of nitrogen in all of the samples shows unequivocally that a copolymerization process does in fact occur, since the nitrogen-containing monomer (vinylcaprolactam) does not polymerize to any significant extent under these conditions. One of the most characteristic samples (Experiment 4, Table 1) was subjected to selective dissolution (in alcohol and water): the copolymer dissolved completely in alcohol, which indicated the absence of any pure methyl methacrylate polymer, and it was completely insoluble in water, which indicates the absence of the water-soluble polymer of vinylcaprolactam. The product of Experiment 4, therefore, was a copolymer of methyl methacrylate and vinylcaprolactam, without any appreciable admixture of the polymers of the original monomers.

Table 2 gives the principal results on the copolymerization of vinylcaprolactam and methyl methacrylate in presence of the azo nitrile. The properties of the copolymers obtained vary in the same direction as those of the copolymers obtained in presence of benzoyl peroxide; the yields, however, vary in a somewhat different way.

In order to prove that the products consisted of copolymers, and were not mixtures of two polymers, their behavior toward various solvents was studied (Table 3).

It will be seen from Table 3 that the solubility of these copolymers differs in character from the solubility of the corresponding polymers. As the proportion of vinylcaprolactam units in the copolymers increases, solubility in benzene, alcohol, and water increases. It should be noted that individual samples of similar composition do not correspond completely in their solubility relations, but the variation in such products is not unduly great. This fact must be borne in mind when inferences are made about the compositions of copolymers merely on the basis of the results of selective dissolution.

Tables 5 and 6 give results on the fractionation of some of the samples, and it will be seen that the copolymers are not homogeneous in composition: fractions having a nitrogen content of less than 5% are insoluble in water, but still soluble in alcohol, and fractions containing less than 3% of nitrogen are insoluble in alcohol.

The results that we have described indicate that a process of copolymerization occurs between vinylcaprolactam and methyl methacrylate, both in presence of benzoyl peroxide, and also in presence of 2,2'-azobis[2-methyl-

TABLE 1

Yields and Compositions of Copolymers of Vinylcaprolactam (VCL) and Methyl Methacrylate (MMA) (Catalyst: Benzoyl Peroxide)

Expt. No.	Composition of original mixture (mole-%)		Yield of copolymer (%)	η_{rel}*	N content of copolymer (%)	Proportions of monomer units (%)	
	MMA	VCL				MMA	VCL
1	100	–	94.2	–	–	100	–
1a	96	4	93.6	2.268	Traces	Not calculated →	
2	75	25	75.8	2.288	1.95	85.23	14.73
3	50	50	53.6	2.880	2.28	82.6	17.4
4	25	75	25.8	1.807	4.27	65.8	34.2
5	5	95	9.6	1.234	6.55	42.6	57.4
6	–	100	–	–	–	–	–

* The viscosities were measured for benzene solutions containing 1 g of polymer per 100 ml of benzene.

TABLE 2

Yields and Properties of Copolymers (Catalyst: 2,2'-Azobis [2-methylpropionitrile]

Expt. No.	Composition of original mixture (mole-%)		Yield of copolymer (%)	η_{rel}*	N content of copolymer (%)	Proportions of monomer units (%)	
	MMA	VCL				MMA	VCL
8	100	0	94.2	–	–	100	–
8a	95	5	98.0	1.771	Traces		Not calculated
9	75	25	80.1	1.970	1.95	85.7	14.3
10	50	50	77.0	2.158	4.06	67.1	32.9
11	25	75	60.0	1.536	6.69	40.75	59.25
12	5	95	76.4	1.274	7.87	27.6	72.4
14	0	100	79.6	1.172	9.72	–	100

* The viscosities were measured for benzene solutions containing 1 g of polymer per 100 ml of benzene.

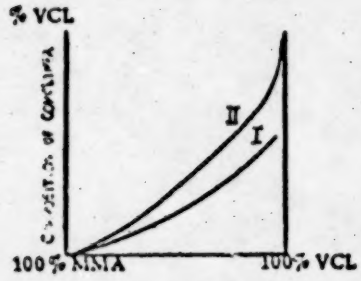
TABLE 3

Solubilities of Copolymers of Vinylcaprolactam and Methyl Methacrylate Formed in Presence of 2,2-Azobis [2-methylpropionitrile]

Name of polymer	Composition of copolymer (mole-%)		Solvent*				
	MMA	VCL	acetone	diethyl ether	benzene	ethanol	water
Polymer of MMA	100	–	+	–	–	–	–
Copolymer 8a	Not Calculated →		+	–	⊥	T	–
Copolymer 9	85.7	14.3	+	–	⊥	T	–
Copolymer 10	67.1	32.9	+	–	+	T	T
Copolymer 11	40.75	59.25	+	–	+	T	T
Copolymer 12	27.6	72.4	+	–	+	+	T
Polymer of VCL	–	100	+	–	+	+	+

* + soluble; ⊥ sparingly soluble; – insoluble; T partially soluble.

propionitrile], no evidence of the formation of the single-component polymers was obtained. In both cases the composition of the copolymer depends on the proportion of monomers in the original mixture, and the proportion of vinylcaprolactam units in the copolmer is less than in the original monomeric mixutre. This difference in composition is more marked in copolymers prepared in presence of benzoyl peroxide (see graph).



Dependence of the composition of the copolymer on that of the monomeric mixture: I) benzoyl peroxide catalyst; II) azo nitrile catalyst.

Under similar conditions, the yield of copolymer is less in the process initiated by benzoyl peroxide than in the process initiated by the azo nitrile. The results confirm that the tendency to undergo copolymerization, like the tendency of the individual monomers to undergo polymerization, depends not only on the reaction mechanism, but also on the character of the initiator used. The reaction that we have studied permits us, on the one hand, to establish a relationship between the reactivities of vinylcaprolactam and methyl methacrylate, and on the other, to synthesize new macromolecular compounds having interesting properties.

EXPERIMENTAL

The starting materials were freshly distilled and were characterized by the following constants: methyl methacrylate, b.p. 100.5°, n_D^{20} 1.4150; d_4^{20} 0.9361; vinylcaprolactam, b.p. 94-95° (4 mm) and n_D^{20} 1.5135; benzoyl peroxide was reprecipitated twice from chloroform solution by means of methanol. 2,2'-Azobis [2-methylpropionitrile] was recrystallized twice from methanol.

The polymerizations were carried out in sealed tubes in presence of 0.2% of initiator and at a temperature of 60 ± 1°. The monomers were taken in various proportions (total weight of mixture 5 g). Reaction was allowed to proceed continuously until solid or highly viscous materials were obtained (72 hours for benzoyl peroxide, 48 hours for the azo nitrile). At the end of the reaction the tubes were cooled to 0°. Control experiments on the polymerization of the monomers were carried out under the same conditions. The polymeric products were dissolved in benzene or acetone, precipitated with diethyl ether, and washed repeatedly with precipitant until tests for double bonds were negative. Precipitant was removed by decantation, and the polymers were dried to constant weight at a residual pressure of 5-6 mm and a temperature of 55-60°. They were analyzed for nitrogen content•. The solutions remaining after the precipitation of the copolymers were fractionated in order to determine the amounts of unchanged monomers.

TABLE 4

Expt. No.	Composition of original mixture (mole-%)		Weight of copolymer (g)•	Amount of vinyl-caprolactam isolated (g)	Weight of undistilled residue (g)
	MMA	VCL			
1a	95	5	4.7	–	0.1
2	75	25	3.79	0.8	–
3	50	50	2.68	1.6	0.2
4	25	75	1.30	2.0	0.8
5	5	95	0.48	2.38	1.50
6	–	100	None	4.7••	–

• Original weight of monomer mixture 5 g.

•• Redistillation of Sample No. 6 yielded 4.2 g of pure vinylcaprolactam and 0.4 g of resinous residue.

Copolymerization in Presence of Benzoyl Peroxide

The copolymerization was carried out by the procedure described above. The balance sheet of the reaction products is given in Table 4, and their characteristics are given in Table 1.

A sample of Copolymer No. 4 was extracted repeatedly with water, separated from the water, and dried to constant weight in a vacuum desiccator over calcium chloride. Before extraction the weight of copolymer was 0.6462 g and its nitrogen content was 4.31, 4.20%. After extraction it weighed 0.6352 g and had a nitrogen content of 4.27, 4.18%

• All analyses were carried out in the Microanalysis Laboratory of the Institute of Organic Chemistry of the USSR Academy of Sciences by Savvateeva, Shakurova, and Samokhotova, to whom we extend our thanks.

TABLE 5

Fractionation of Copolymers by Dissolution in Water

Sample No.	Composition of unfractionated Copolymer (mole-%)		Amount taken for fractionation (g)	N content of unfractionated copolymer (%)	Amount extracted by water		Insoluble residue	
	MMA	VCL			(g)	Ncontent (%)	(g)	N content (%)
9	85.7	14.3	1.0741	1.95 1.94	None	–	1.010	Not determined
11	40.75	59.25	1.0676	6.69 6.76	0.4430	7.43 7.38	0.5257	4.42 4.57
12	27.6	72.4	0.5818	7.87 7.83	0.4520	7.48 7.71	0.080	4.34

TABLE 6

Fractionation of Copolymers by Dissolution in Alcohol

Sample No.	Composition of unfractionated copolymer (mole-%)		Amount taken for fractionation (g)	N content of unfractionated copolymer (%)	Amount extracted by alcohol		Insoluble residue	
	MMA	VCL			(g)	N content (%)	(g)	N content (%)
9	85.7	14.3	1.72	1.95 1.94	1.175	2.22 2.33	0.3359	1.05 1.06
10	67.1	32.9	2.15	4.06 4.03	1.759	3.97 3.83	0.2928	1.84 1.81
12	27.6	72.4	2.0	7.87 7.83	1.835	8.20 7.97	None	–

Copolymerization in Presence of 2,2-Azobis [2-methylpropionitrile]

The results of the experiments are given in Table 2. Data on the fractionation are given in Tables 5 and 6.

SUMMARY

1. A study was made of the copolymerization of vinylcaprolactam with methyl methacrylate in presence of benzoyl peroxide and of 2,2'-azobis [2-methylpropionitrile].

2. The copolymers obtained were characterized by their elementary compositions, viscosities, and solubilities.

3. It was shown that the yields and compositions of the copolymers depend on the proportion of reactants in the monomeric mixture.

4. Selective-dissolution experiments showed that the copolymers were not homogeneous in composition. No single-component polymers were detected.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 79. PRODUCTS OF THE POLYCONDENSATION OF DIALDEHYDES AND DIKETONES WITH DIAMINES AND GLYCOLS

V. V. Korshak and S. V. Vinogradova

Dialdehydes, diketones, and keto acids all have very reactive carbonyl groups, which readily react with amines, alcohols, and other compounds containing mobile hydrogen atoms. The ability of carbonyl compounds, such as aldehydes, to undergo these reactions has found practical application for a long time in the preparation of synthetic resins, for example, the three-dimensional condensation products of formaldehyde with phenols, aniline, urea, and other substances. An extensive literature is devoted to the study of these reactions [1]. However, the use of carbonyl compounds for the preparation of linear polymers has remained almost without investigation, except in a few studies, which we shall now discuss briefly. With the object of preparing linear polymers Korshak and Pozhiltsova [2] investigated the reaction of (4,4'-biphenylene) dihydrazine with 2,4-pentanedione, 2,3-butanedione, and terephthalaldehyde and obtained the first members of the class of polyhydrazones; at the same time they showed that the molecular weight of the polyhydrazone is reduced by the presence of excess of one of the reactants. Erlenmeyer and Büchler [3] obtained linear polymers containing thiazole nuclei by the polycondensation of the dithio amides of adipic, azelaic, and oxalic acids with dihalo diketones, such as 1,4-dibromo-2,3-butanedione, 1,8-dichloro-2,7-octanedione, and 1,11-dichloro-2, 10-undecanedione. Krässig and Greber [4] prepared condensation products of terephthalaldehyde with various diamines of the type $NH_2(CH_2)_n - X - (CH_2)_nNH_2$, in which X = O or NH, which they considered to be cyclic substances having rings of 26-30 atoms, without giving any proof in support of their view. Franke and Gigerl [5], and later Carothers [6], showed that aldehydes react with glycols with formation of polyacetals.

EXPERIMENTAL

The object of the present investigation was to bring about reaction between various bifunctional carbonyl compounds with diamines and glycols in order to determine whether linear polymers could be prepared. For this purpose reactions were carried out between 1,6-hexanediamine and carbonyl compounds, such as 2,3-butanedione, 2,4-pentanedione, pyruvic acid, and terephthalaldehyde, and also the reaction of the last compound with ethylene glycol and with 1,6-hexanediol. The products obtained were characterized.

In the reactions between 1,6-hexanediamine and carbonyl compounds, the reactants were taken in a molar ratio of 1 : 1; the reactions were carried out in an atmosphere of nitrogen, and heat was applied. Heat was not applied until the reactants had been mixed together, and reaction sometimes began in the cold with evolution of heat so that a certain amount of cooling had to be applied at first. The temperature of the mixture was raised gradually to 180° in the case of terephthalaldehyde, and to 110° in all other cases. The duration of the heating was 11-20 hours. The stream of nitrogen was then turned off and the mixture was heated further for 8-15 hours at a residual pressure of 1-2 mm. The properties of the products are given in Table 1.

The reactions between 1,6-hexanediamine and the carbonyl compounds listed in Table 1 result in the formation of polymers, which may be either solid or liquid, depending on the nature of the original reactants. When we arrange the original reactants in order of the melting points of the polymers that they form, we obtain the following series: 2,4-pentanedione, pyruvic acid, 2,3-butanedione.

These changes in melting point can be correlated with changes in solubility. The condensation product from 2,4-pentanedione is considerably more soluble in an alcohol-chloroform mixture than the products formed by 2,3-butanedione and by pyruvic acid. Here we can clearly see the effect of the methylene group separating the two carbonyls in 2,4-pentanedione in lowering the melting point and raising the solubility.

When the condensation product from 1,6-hexanediamine and terephthalaldehyde is not given the vacuum

treatment it is still soluble in cresol, but after being heated in a vacuum it becomes insoluble in all organic solvents, though it is dissolved by dilute hydrochloric acid, which evidently brings about its degradation.

TABLE 1

Second component	Properties of reaction product				Appearance and solubility
	M.p. (°C)	Elementary analysis (%)			
		C	H	N	
Terephthalaldehyde	188-192	76.50	8.49	10.23	Clear reddish solid. Insoluble in organic solvents
		76.58	8.65	10.12	
2,3-Butanedione	Does not melt	72.31	10.11	13.68	Dark-colored solid, soluble in an alcohol-chloroform mixture
		72.12	10.16	13.44	
2,4-Pentanedione	Vaseline-like	67.69	10.59	14.31	Viscous reddish mass
		67.70	10.56	14.43	
Pyruvic acid	76-85	59.22	9.40	12.73	Dark-colored solid, soluble in an alcohol-chloroform mixture
		59.43	9.53	12.76	

TABLE 2

Empirical formula	Degree of polymerization	Content (%)		
		C	H	N
$C_{22}H_{36}O_2N_2$	1	75.43	7.43	8.00
$C_{36}H_{68}O_3N_6$	2	76.49	8.07	9.82
$C_{50}H_{66}O_3N_6$	3	76.73	8.44	10.74
Found	–	76.50	8.49	10.23
	–	76.58	8.65	10.12

No special experiments were made to determine the structures of the products that we had obtained, but the results of elementary analysis lead us to suppose that they were formed as a result of reaction between the amino groups of the 1,6-hexanediamine and the carbonyl groups of the second component. It is known that the first stage of the reaction of an aldehyde or ketone with an amine or amide is the formation of a hydroxyl-containing condensation product in accordance with the scheme:

$$RCH{=}O + H_2NR' \rightarrow RCH(OH)NHR'.$$

When heated, and sometimes in the cold, this product loses water with formation of an unsaturated compound in accordance with the scheme:

$$RCH(OH)NHR' \rightarrow H_2O + RCHNR'.$$

Carbon, hydrogen, and nitrogen determinations on our products showed that they were substances of the second type, formed by elimination of water. The products were of low molecular weight. For example, the condensation product from terephthalaldehyde and 1,6-hexanediamine was found to have a molecular weight lying between 600 and 800, its probable structure being as follows:

$$O{=}HCC_6H_4CH{=}[{=}NH(CH_2)_4NH{=}CHC_6H_4CH{=}]_x{=}O.$$

in which x lies between 2 and 3. It is most probable that the product was a mixture of molecules having degrees of

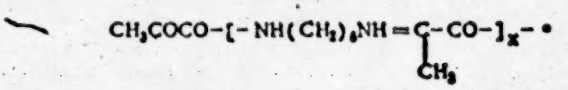
• This formula and the empirical formulas and calculated C, H, and N contents given in Table 2 are here presented exactly as in the original. It will be clear, however, that the hydrogens attached to the nitrogens should be omitted from the formula, and the formulas and figures in Table 2 need to be corrected accordingly. The entries in Table 2 should read $C_{22}H_{24}O_2N_2$, 75.86% C, 6.90% H, 8.05% N; $C_{36}H_{48}O_2N_4$, 76.67% C, 7.47% H, 9.97% N; $C_{50}H_{66}O_2N_6$, 77.32% C, 7.73% H, 10.82% N; as in the original, calculations are based on integral atomic weights. There is a similar error in the formula for the pyruvic acid condensation product, in which the hydrogen on the second nitrogen should be omitted. With this correction the empirical formula for $x = 2$ is $C_{24}H_{34}O_2N_4$, for which the analysis should be (%): C 69.43; H 8.49; N 13.21. — Publisher.

polymerization of 2 and 3. Table 2 gives carbon, hydrogen, and nitrogen contents calculated for different values of the degree of polymerization.

Owing to its high volatility, 1,6-hexanediamine was lost in the course of the reaction to a greater extent than the aldehyde: this explains the fact that the terminal groups were aldehyde residues.

In view of the structure that we have proposed for the condensation products, we must give some consideration to the work of Krässig and Greber [4], who assigned a cyclic structure (30-membered ring) to substances formed by the condensation of terephthalaldehyde with 3,3-oxybispropylamine. The impossibility of the formation of such rings as the result of a condensation process is quite obvious from stereochemical considerations, and these authors gave no experimental proof of their proposed structure in their paper.

The structure of the condensation product from 1,6-hexanediamine and pyruvic acid may be represented by an analogous formula:



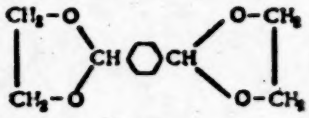
in which $x = 2$, as can be readily seen by comparison of the analytical figures for the product with the calculated figures for the above formula:

Found %: C 59.22; 59.43; H 9.40; 9.53; N 12.73; 12.76

$C_{21}H_{34}O_3N_4$. Calculated %: C 59.15 H 8.92; N 13.14

In the reactions with 2,3-butanedione and 2,4-pentanedione, products were obtained having nitrogen contents that differed appreciably from the calculated values, which must be associated with the high volatility of the reactants and their tendency to undergo oxidation, particularly during the long period of heating. There can be no doubt, however, that here also the products were of low molecular weight and had similar structures.

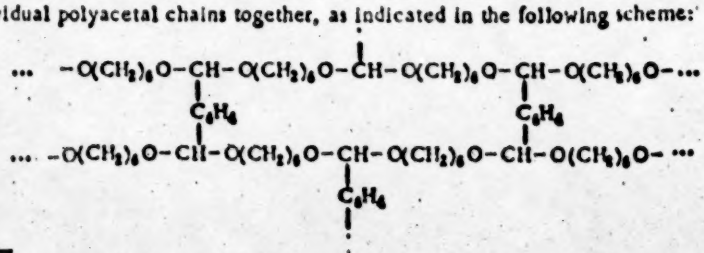
A different result was obtained in the reactions of terephthalaldehyde with glycols. In the reaction with ethylene glycol no macromolecular products were formed, but a cyclic diacetal of terephthaladehyde and ethylene glycol was obtained:



This diacetal is a white crystalline substance melting at 79-80°.

In this case, as in others in which a five- or six-membered ring can be formed, cyclization predominates over linear-polymer formation, so that a cyclic product is obtained – in this case the diacetal of terephthalaldehyde. The reaction of terephthalaldehyde with 1,6-hexanediol resulted in the formation of a three-dimensional polyacetal. The product was an elastic rubberlike mass, insoluble in organic solvents. Its dissolution could be effected only with cresol, which evidently degraded the three-dimensional polymer, since the solutions obtained were of low viscosity.

The formation of a three-dimensional polymer becomes quite understandable when it is remembered that the reaction of glycols with monoaldehydes results in the formation of linear polyacetals, which was shown by Franke and Gigerl [5], and also by Carothers [6]. As terephthalaldehyde contains two aldehyde groups, its reaction with 1,6-hexanediol leads to the formation of a three-dimensional network in which phenylene groups act as bridges linking individual polyacetal chains together, as indicated in the following scheme:



• See previous footnote. — Publisher.

We attempted to modify the polyacetal in order to increase its solubility: we added octyl alcohol to the reaction mixture and then heated it. However, the attempt was not successful: the product was insoluble, and was similar to that obtained in absence of the monohydric alcohol.

SUMMARY

1. It was shown that, in the reactions of 1,6-hexanediamine with terephthalaldehyde, with 2,3-butanedione, with 2,4-pentanedione, and with pyruvic acid, condensation products of similar structure are formed.

2. It was found that reaction of terephthalaldehyde with ethylene glycol results in the formation of a cyclic diacetal, whereas its reaction with 1,6-hexanediol gives a three-dimensional polyacetal.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 80. A CASE OF MIGRATIONAL COPOLYMERIZATION

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Migrational polymerization is a polymerization process characterized by the occurrence of hydrogen transfer in each elementary act of the reaction [1]. Polymerization reactions of this type, which has received very little study, include the copolymerization of diisocyanates and glycols [1] and the copolymerization of diolefins, such as 1,5-hexadiene, 2,6-diallylphenylacetate, 1,6-heptadien-4-ol, and 1,5-diphenyl-3-pentadienone with various dithiols [2].

An interesting reaction in this connection is that of the addition of alcohols and amines to the double bond in various acrylic and methacrylic derivatives. It is known that acrylonitrile [3], acrylic acid [4], and methacrylic esters [5] readily combine at the double carbon-carbon bond with alcohols, thiols, amines, and other compounds having mobile hydrogen atoms and form addition products (derivatives of 3-substituted propionic acid):

$$ROH + CH_2 = CHCOOR' \rightarrow RO-CH_2CH_2COOR'.$$

In this paper we give the results of preliminary experiments in which it was shown that polymers may be obtained by the addition of glycols, diamines, and amino alcohols to diacrylic or dimethacrylic esters of glycols.

EXPERIMENTAL

The unsaturated compounds used were ethylene diacrylate, ethylene dimethacrylate, and hexamethylene dimethacrylate, which were prepared by heating a mixture of the appropriate acid and glycol in presence of sulfuric acid, benzene, and an inhibitor (hydroquinone). Addition reactions were carried out between these acrylic and methacrylic esters and 1,6-hexanediamine, ethylene glycol, and 1,3-diamino-2-propanol.

Experimental Procedure

Mixtures of reactants were prepared in glass tubes, which were freed from air by repeated sequences of evacuation and filling with pure nitrogen, and then sealed. The sealed tubes were then placed in a thermostat, which maintained the temperature within the required range. An inhibitor was present in each tube, hydroquinone and dinitrobenzene being used for this purpose. Inhibitors were used in order to avoid the occurrence of radical polymerization. A control experiment was included in each series, the tube then containing only the diacrylic or dimethacrylic ester and inhibitor. No polymerization occurred in the control experiments, so that the formation of polymer in the other tubes was to be attributed to migrational, not radical polymerization.

Copolymerization with 1,6-Hexanediamine

The experiments on the copolymerization of 1,6-hexanediamine with ethylene dimethacrylate, with ethylene diacrylate, and with hexamethylene dimethacrylate were carried out at 50°, 110°, and 150° at molar ratios of ester to diamine of 1 : 1 and 1 : 0.5 and for various periods of time (from a few hours to 80 hours).

The products obtained at 50° with a heating period of up to 80 hours were clear colorless plastic substances, readily soluble in acetic acid and in an alcohol-chloroform mixture. The products obtained at 110° were soluble only when heating was for not more than nine hours. Further heating resulted in the formation of clear colorless substances that were not soluble. The products obtained at 150° were soluble only when heating was for not more than three hours, more prolonged heating resulting in the formation of insoluble substances. Reaction with ethylene diacrylate was more rapid than with ethylene dimethacrylate.

The product obtained by reaction of 1,6-hexanediamine with an equimolecular amount of ethylene dimethacrylate at 150° for 17 hours was washed with alcohol, water, and ether, and then dried. A powder was obtained which

was insoluble in organic solvents; its elementary composition was (%): C 60.42; 60.38; H 9.63; 9.74; N 9.40; 9.41

The linear reaction product in the copolymerization of 1,6-hexanediamine with ethylene dimethacrylate in accordance with the equation:

$$x\,CH_2=C(CH_3)COO(CH_2)_2OOCC(CH_3)=CH_2 + x\,H_2N(CH_2)_6NH_2 \rightarrow$$
$$\rightarrow\{-CH_2-CH(CH_3)COO(CH_2)_2OOCCH(CH_3)CH_2-NH(CH_2)_6NH-\}_x.$$

would have the composition (%): C 61.11; H 9.55; N 8.91. The somewhat higher carbon content suggests that the analyzed product was a three-dimensional polymer and had extra ethylene dimethacrylate units incorporated in its structure.

The formation of soluble polymers in the first stages of the reaction and their conversion into three-dimensional polymers during further heating indicate that at first only one hydrogen of the amino group reacts, but at a later stage the second hydrogen also reacts.

Copolymerization with Ethylene Glycol

The experiments on the copolymerization of ethylene glycol with ethylene dimethacrylate and with ethylene diacrylate were carried out at 50° and at 110° in presence of the sodium derivative of the glycol (2.5% or 5% on the weight of ethylene glycol) as catalyst. Reaction times of up to 140 hours were used.

The reaction products were clear liquids, readily soluble in acetic acid and in an alcohol-chloroform mixture. The reaction product obtained by heating ethylene dimethacrylate with an equimolecular amount of ethylene glycol for 100 hours in presence of 2.5% of the sodium derivative of the glycol was treated with water to remove catalyst, washed with ether, carefully dried, and analyzed with the following results (%): C 55.48; 55.70; H 7.02; 6.97.

The polymer would be expected to have the following structure:

$$(-OCH_2CH_2OCH_2CH(CH_3)COOCH_2CH_2OOCCH(CH_3)CH_2-)_x.$$

Its analysis should be (%): C 55.37; H 7.69. It will be seen by a comparison of the determined and calculated carbon and hydrogen contents that the polymer obtained was a copolymer of ethylene glycol and ethylene dimethacrylate of the structure given above.

One of the products obtained by reaction between ethylene diacrylate and ethylene glycol was purified in a similar way and analyzed with the following results (%): C 51.68; 51.63; H 6.66; 6.45. For the expected polymer $(-OCH_2CH_2OCH_2CH_2COOCH_2CH_2OOCCH_2CH_2-)_x$ the analysis should be (%): C 51.72; H 6.89. For the copolymer of ethylene glycol with ethylene diacrylate the determined and calculated carbon and hydrogen contents are in sufficiently close agreement.

Copolymerization with 1,3-Diamino-2-propanol

Experiments on the copolymerization of 1,3-diamino-2-propanol with ethylene dimethacrylate and with ethylene diacrylate were carried out at various molar ratios (from 1 : 1 to 2 : 5) at 110° for 30 hours (of which 13 hours were under vacuum conditions). In some experiments an additional 2.5 % of the sodium derivative of 1,3-diamino-2-propanol was made, as catalyst. In all cases transparent, slightly greenish or yellowish, somewhat elastic solids, insoluble in organic solvents, were obtained as products. The hardest products were obtained when the molar ratio of reactants was 1 : 1.

DISCUSSION OF RESULTS

It may be inferred from the results that the acrylic and methacrylic esters of ethylene glycol and 1,6-hexanediol are able to undergo copolymerization with diamines, glycols, and amino alcohols. The reaction leads to the formation of linear and three-dimensional compounds, which are polyesters in which ether or imino linkages alternate with ester groupings. Polymers of this type were previously unknown; they may be prepared also by the polycondensation of ethylene glycol or 1,6-hexanediol with dicarboxylic acids containing ether or imino linkages in their chains.

The copolymerization of acrylic and methacrylic esters with glycols belongs to a type of polymerization processes that closely resemble the copolymerization reactions between glycols and diisocyanates. Reactions of this type are characterized by the occurrence of hydrogen transfer in each elementary act of the reaction. It is therefore desirable to refer to this type of reactions as "migrational copolymerization", as suggested by one of us and Gribova [6].

SUMMARY

1. The reactions of 1,6-hexanediamine with ethylene dimethacrylate, with hexamethylene dimethacrylate, and with ethylene diacrylate were investigated.

2. The reactions of ethylene diacrylate and of ethylene dimethacrylate with ethylene glycol and with 1,3-diamino-2-propanol were investigated.

3. It was found that, in the reaction of the acrylic and methacrylic esters of glycols with glycols, diamines, and amino alcohols, copolymers are formed by the mechanism of migrational copolymerization.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 81. MIXED POLYAMIDES CONTAINING GLUTARIC OR PIMELIC ACID RESIDUES

V. V. Korshak and T. M. Frunze

We have previously described mixed polyamides prepared by the polycondensation of 1,6-hexanediamine with mixtures of various proportions of two dicarboxylic acids [1]. The mixed polyamides investigated contained residues of succinic, adipic, suberic, azelaic, and sebacic acids, which, apart from azelaic acid, contain even numbers of carbon atoms in their molecules. The results obtained, therefore, did not give a sufficiently clear picture of the effect of the evenness or oddness of the number of carbon atoms in the dicarboxylic acid on the properties of the polyamides obtained.

With the object of making a more detailed investigation of the effect of the presence of a dicarboxylic acid residue having an odd number of carbon atoms on the properties of mixed polyamides, we have prepared mixed polyamides containing glutaric or pimelic acid residues together with residues of dicarboxylic acids such as adipic, azelaic, and sebacic, present in various proportions.

In the polycondensation experiments and in the investigation of the products the procedure was the same as that used in previous investigations [1, 2]. The dicarboxylic acids used had the following constants: glutaric acid, m.p. 97-98° (the literature [3] gives 97° and 98°), and pimelic acid, m.p. 104-105° (the literature [4] gives 105-105.5). The 1,6-hexanediamine salts of glutaric and pimelic acids were prepared by the method described previously [1] and had the following constants: 1,6-hexanediamine glutarate, m.p. 150°, and 1,6-hexanediamine pimelate, m.p. 161-162°. The other dicarboxylic acids and their 1,6-hexanediamine salts had the constants given previously [1].

DISCUSSION OF RESULTS

The mixed polyamides that we prepared were white opaque horny substances. They could be readily spun from the melt into fibers capable of being cold-drawn. They were very sparingly soluble in ethanol. The dependence of the melting points of the polyamides on their compositions is shown in Table 1.

Table 1 shows that polyamides in which one original component is glutaric or pimelic acid have melting points that vary with composition: the curves for this variation have minima as in the systems investigated previously [1, 2]. This dependence of melting point on the original proportions of reactants is shown graphically in Figures 1 and 2.

The products having the lowest melting points contain a mole fraction of 0.6 of the "odd" acid residue. The low melting points of polyamides derived from odd dicarboxylic acids are to be explained by the fact that not all of the amide groupings in the macromolecular chain are able to interact with amide groupings of neighboring chains with formation of hydrogen bonds. This fact, first noted by Hill and Walker [5], was considered in detail by us in the preceding communication, and in the same paper we demonstrated the effects of even and odd numbers of carbon atoms in the dicarboxylic acid molecule and the effects also of such factors as the chain length of the dicarboxylic acid, diamine, or amino acid.

It was found that with increase in the chain length of the dicarboxylic acid, diamine, or amino acid, the extent of hydrogen bonding between amide groupings of different macromolecules increased. Thus it therefore follows that in in 5,7-nylon $[-NH(CH_2)_5NH-CO(CH_2)_5CO-]_x$ only 50.21% of the amide groupings were found to be capable of forming hydrogen bonds with neighboring macromolecules, whereas in 5,13-nylon $[-NH(CH_2)_5NH-CO(CH_2)_{11}CO-]_x$ the number of hydrogen-bonded amide groupings had risen to 75.32% [6]. Hence, lengthening of the molecules of the reactants, i.e. of the repeating unit of the macromolecule, results in the facilitation of the formation of hydrogen bonds between amide groupings. It may be expected, therefore, that, when the repeating unit is sufficiently long, even polyamides derived from an odd diamine and an odd dicarboxylic acid will be able to form fully hydrogen-bonded systems in which all the amide groupings take part in hydrogen bonding. There will then be complete agreement between the melting points calculated from our proposed formula [7]:

$$y = 7x + 110,$$

(y is the melting point of the polyamide; x is the percentage of the amide groupings that are hydrogen-bonded) and the experimentally observed melting points of the polyamides.

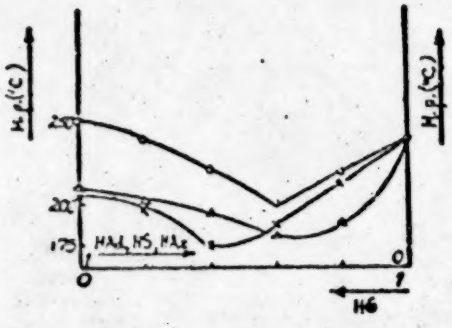


Figure 1

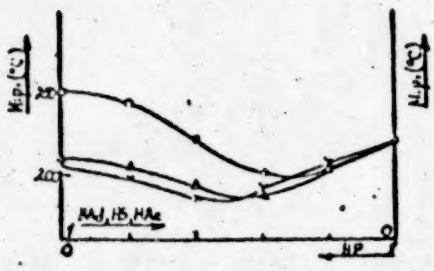


Figure 2

TABLE 1

Melting Points of Mixed Polyamides (°C)

Molar ratio of reactants ••	Names of reactants					
	HAd• / HG	HAz / HG	HS / HG	HAd / HP	HAz / HP	HS / HP
1.0/0.0	250-252	205-208	210-212	250-252	205-208	210-212
0.8/0.2	240-241	199-200	202-205	244-246	197-199	205-208
0.6/0.4	220-222	176-178	195-197	221-222	186-188	193-195
0.4/0.6	200-202	188-189	180-183	200-202	191-192	188-189
0.2/0.8	220-221	214-215	185-187	204-206	205-209	203-205
0.0/1.0	240-241	240-241	240-241	220-225	220-225	220-225

• Abbreviations: Ad adipic acid; Az azelaic acid; S sebacic acid; G glutaric acid; P pimelic acid; H 1,6-hexanediamine.

•• The numerator and denominator refer, respectively, to the salts indicated in the numerator and denominator under the heading "Names of reactants".

Examination of Figures 1 and 2 shows that in systems derived from adipic acid (HAd–HG and HAd–HP) the minimum melting points are the same, although, in view of the difference in the chain lengths of glutaric and pimelic acids, a difference would be expected. Comparison of the melting points of the systems HAz–HG and HAz–HP and also of HS–HG and HS–HP shows that in these cases the lower minimum temperatures are found in the systems containing glutaric acid residues, not pimelic acid residues, although analogy with previous results would lead one to expect the opposite.

It is probable that these discrepancies in the values of the melting points are to be explained on the basis of the considerations already given in which the melting point is associated with the possibility of the formation of a larger or smaller number of hydrogen bonds, which in its turn depends on the length of the repeating unit of the macromolecule. As pimelic acid has a longer chain than glutaric acid, the opportunities for hydrogen bonding between amide groupings will be greater in the polyamides containing the longer pimelic acid. Hence, up to a certain limit, the melting points of polyamides containing a certain proportion of glutaric acid residues will be lower than those of polyamides derived from pimelic acid.

In the glutaric acid systems investigated the highest minimum m.p. was found in the system HAd-Hg, the lowest in the system HAz-HG, and the minimum m.p. of the system HS-HG is intermediate. The pimelic systems present a similar picture; the system HAd–HP has the highest and the system HAz–HP the lowest minimum melting points, and the system HS–HP is intermediate. Hence, in all cases, the lowest minimum melting point is found in systems derived from two dicarboxylic acids having odd numbers of carbon atoms or methylene groups in their molecules.

TABLE 2

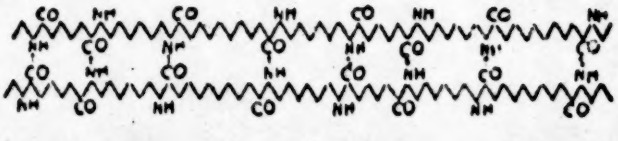
Variation in the Number of Amide Groupings and Number of Hydrogen Bonds (per 100 Methylene Groups) with Variation in the Composition of Mixed Polyamides

Names of reactants*	Molar ratio of reactants	Melting point of polyamide (°C)	Number of amide groupings per 100 methylene groups	Melting point calculated from proportion of amide groupings (°C)	Number of hydrogen-bonded amide groupings per 100 methylene groups	Percent of the amide groupings that are hydrogen-bonded
HAd/HS	1.0/0.0	250	20.00	250	20.00	100.0
"	0.8/0.2	220	18.52	240	15.72	84.83
"	0.6/0.4	190	17.24	230	11.43	66.29
"	0.5/0.5	190	16.66	226	11.43	68.60
"	0.4/0.6	185	16.13	223	10.71	66.39
"	0.2/0.8	190	15.15	216	11.43	75.44
"	0.0/1.0	210	14.28	210	14.28	100.0
HAd/HP	1.0/0.0	250	20.00	250	20.00	100.0
"	0.8/0.2	244	19.60	247	19.14	97.65
"	0.6/0.4	221	19.23	245	15.85	82.46
"	0.4/0.6	200	18.86	242	12.85	68.13
"	0.2/0.8	204	18.51	239	13.43	72.55
"	0.0/1.0	220	18.18	237	15.71	86.41
HAz/HP	1.0/0.0	205	15.33	217	13.58	88.23
"	0.8/0.2	197	15.87	221	12.43	78.32
"	0.6/0.4	186	16.39	225	10.85	66.19
"	0.4/0.6	191	16.94	228	11.57	68.23
"	0.2/0.8	205	17.54	233	13.57	77.36
"	0.0/1.0	220	18.18	237	15.71	86.41

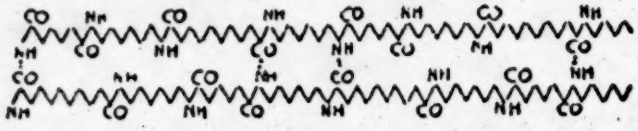
* The abbreviations are the same as in Table 1.

The question of the causes of the low melting points of mixed polyamides as compared with the melting points of single-component polyamides prepared from the same original substances, was considered by us previously [1, 2]. The proposed explanation was based on the assumption of an irregular distribution of units of different structure along the length of the macromolecular chain - this assumption being based on analogy with copolymers of the vinyl type. The possibility of the irregular distribution of units of different structure along the length of the macromolecular chain is quite a feasible one. Thus, we have shown that mixed polyamides of identical composition may have melting points that differ according to the duration of heating, i.e. according to the completeness with which polycondensational equilibrium is attained [8]. At the same time, the fact that we can obtain mixed polyamides of identical composition and identical melting point in different experiments shows that it is quite possible to attain identical states representing fairly complete polycondensational equilibrium. The regularity of the distribution of the units will then be at its maximum. It is then necessary to seek the cause of the presence of a minimum on the melting point curve in the difference of the arrangement of the macromolecular chains. In order to examine this matter we calculated the numbers of amide groupings and hydrogen bonds (per 100 methylene groups) in polyamides of various compositions (Table 2).

For simplicity we shall first examine the case of the system HAd–HS at a molar ratio of 1 : 1. When complete equilibrium is attained, it is to be expected that there will be a regular distribution of the different kinds of units along the length of the chain, as shown in the following scheme:



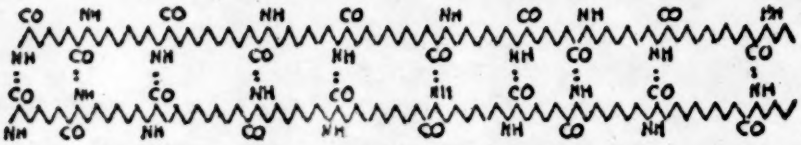
When the mutual disposition of the units of different macromolecules is such that identical units fall together, all amide groupings are able to form hydrogen bonds of the highest stability (dotted lines). Hence, with such a distribution of units it is impossible for the melting point to be lowered and for a minimum to be formed on the melting point curve. However, for a mixed polyamide of this composition another distribution of units of the macromolecules is possible and is shown in the following scheme:



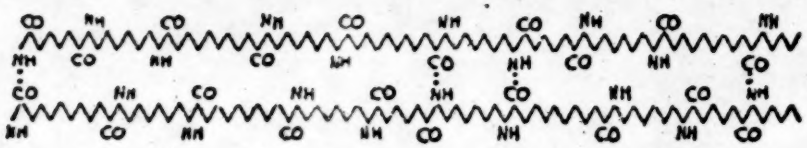
In this case only one-half of the amide groupings can form hydrogen bonds with neighboring macromolecules. If it is assumed that the two arrangements of macromolecules are equally probable, then we can estimate that roughly 75% of the amide groupings are hydrogen-bonded. According to our calculations (Table 2), the actual proportion is 68.60%. When it is considered that our calculations do not take a large number of steric factors into account, the agreement can be regarded as satisfactory.

These considerations retain their significance whatever may be the proportions of the reactants, but in addition we then have the effect of the irregular structure of the macromolecule along the length of its chain. The effect of this factor was considered by us in previous papers [1, 2]. We shall consider here the effect of a combination of the two factors.

In the system HAd–HS, molar ratio 2 : 3, the units of the macromolecular chain are distributed less regularly, as shown in the following scheme:

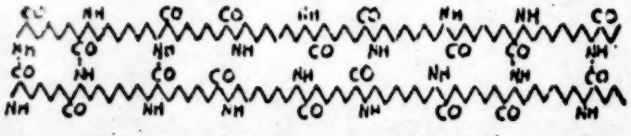


Here again, however, it is possible to arrange the macromolecules so that all of the amide groupings are hydrogen-bonded, in the manner shown. But for any other relative disposition of the macromolecules the extent of hydrogen bonding is reduced greatly, as shown in the following scheme:

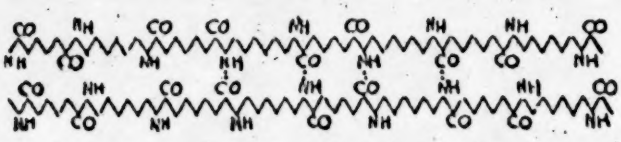


It now becomes clear why polyamides prepared from the reactants in the molar ratio of 2 : 3 have much fewer opportunities of hydrogen bonding. The data in Table 2 show that the proportion of the amide groupings that are hydrogen-bonded is practically the same for the molar ratio 2 : 3 as for the ratio 3 : 2, but the absolute numbers of hydrogen bonds (per 100 methylene groups) are different. The absolute number is less when the longer acid is in excess – in this case sebacic acid – and this explains the occurrence of a minimum on the melting point curve and the position of this minimum.

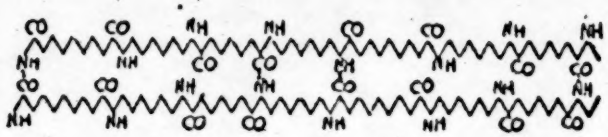
For mixed polyamides derived from odd dicarboxylic acids the picture is still more complicated. Thus, in the system HAd–HP, molar ratio 1 : 1, we may have the following arrangement:



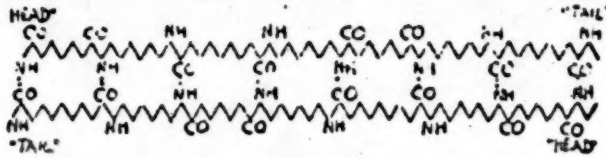
In this case there is no possible disposition of the macromolecules in which all the amide groupings can be hydrogen bonded; thus we have the following arrangement:



In systems derived from two dicarboxylic acids containing odd numbers of carbon atoms – or, what amounts to the same, methylene groups – the mutual dispositions of the macromolecules can be represented (the example taken being the system HAz–HP, molar ratio 1 : 1) as follows:

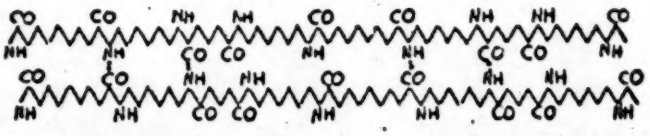


This system, like polycaprolactam, has vector macromolecules, i.e. macromolecules in which the structure reads differently according as we regard the molecule in the direction from left to right or in the reverse direction. It is here possible to form hydrogen bonds with all of the amide groupings when the chains are arranged so that they lie alternately in head-to-tail and tail-to-head directions, as follows:



However, in such a combination only half of the total number of amide groupings are utilized, the other half being disposed in such a way that, as in the preceding scheme, they may form hydrogen bonds only with part of the amide groupings of neighboring macromolecules. Hence, the occurrence of such a disposition of macromolecules that it becomes possible to form an increased number of hydrogen bonds, as indicated in the above scheme, results merely in an increase in the total number of hydrogen bonds in such a mixed polyamide to a value exceeding the calculated value. Thus, from the data given in Table 2 we calculated that the percentage of hydrogen-bonded amide groupings is about 67.21, whereas the first scheme for the disposition of the macromolecules will permit hydrogen bonding only to the extent of 50% or less.

Unlike this system, the system HAz–HO, molar ratio 1 : 1, cannot assume a state in which the disposition of the macromolecules permits hydrogen bonding to the extent of more than 50%. Below we show one of the possible arrangements of the macromolecules of this polyamide, from which it will be seen that in this case 50% of the amide groupings may be hydrogen-bonded:



The same result is obtained when other arrangements of the macromolecules are considered. The percentage of hydrogen-bonded amide groupings calculated from the melting point is 51.87.

The relationship that we have shown to exist between the mutual disposition of the macromolecules of mixed polyamides and the extent of hydrogen bonding provides a basis for an explanation of the strengthening process that occurs during the cold drawing of these materials. During this process the material flows, so that the macromolecules move relative to one another. It then becomes possible for macromolecules to take up positions in which the

intermolecular hydrogen bonding is at a maximum. The macromolecules will become fixed in these mutual positions within the mass of the polyamide. This disposition of the macromolecules corresponds to the moment when the polyamide sample acquires maximum mechanical strength. It is natural that the process of drawing will be accompanied by the straightening of the macromolecules and will result in an oriented arrangement of macromolecules within the materials, which is the main result of this process.

SUMMARY

1. A study was made of binary mixed polyamides derived from 1,6-hexanediamine glutarate or pimelate as one component and 1,6-hexanediamine adipate, azelaate, or sebacate as the other component of the reacting mixture.

2. It was found that the investigated systems had minimum melting points for a content of 60 mole-% of the component having an odd number of carbon atoms in its molecule.

3. The question was considered of the effect of the mutual disposition of the polyamide macromolecules on the extent of the hydrogen bonding of the amide groupings, and it was shown that the extent of hydrogen bonding varies greatly with variation in the mutual dispositions of the macromolecules of mixed polyamides.

4. An explanation was advanced for the occurrence of a minimum on the curve for melting point against composition.

5. It was suggested that the extent of hydrogen bonding in mixed polyamides may change as a result of cold drawing.

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* T.p. = C. B. Translation pagination

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Institute of Heteroorganic Compounds of the USSR Academy of Sciences

MACROMOLECULAR COMPOUNDS

COMMUNICATION 82. 2,4,5-TRIISOPROPYL-α-METHYLSTYRENE

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As shown previously, substituents on carbon atoms linked by a double bond have a hindering effect on the polymerization process, this effect being particularly great when there are numerous bulky substituents [1-5]. The obstacles to the polymerization process are particularly great when four or three substituents are present [6]. However, the presence of only one substituent, if it is bulky and appreciably ramified, is sometimes sufficient to cause great hindrance to the polymerization process. Thus, it was found that 4-tert-butyl-2,6-dimethylstyrene is unable to undergo radical polymerization, though it is still able to polymerize in presence of catalysts acting by the ionic mechanism [7, 8]. When there is only one substituent in the ortho position of the phenyl group the steric hindrance is not so great, as we showed in the case of 2,4,5-triisopropylstyrene, which readily polymerizes, both under the action of initiators and also simply by the action of heat [9].

It was of interest to determine the effect of a substituent such as a methyl group when it is not in the phenyl group but is directly substituted in the vinyl group. There are references to the behavior of such compounds in the literature. It is known, for example, that α-methylstyrene does not readily polymerize by the radical mechanism, though it undergoes ionic polymerization as readily as styrene itself. Bachman and Hellman [10] found that α, 2,3-trimethylstyrene does not polymerize in presence of peroxides, but its ability to undergo ionic polymerization was not examined.

When there are two ortho substituents in the phenyl group and one substituent in the vinyl group, then, as we showed for 4-tert-butyl-α, 2,6-trimethylstyrene and 2,6-dimethoxy-α-methylstyrene, the compounds are not capable of either radical or ionic polymerization. Hence, the presence of two ortho substituents in the phenyl group and one α-substituent in the vinyl group creates great steric hindrance, blocking and screening the vinyl group to such an extent that it loses its ability to react with the similar group of another molecule.

It was of interest to determine the effect of a single ortho substituent in α-methylstyrene for the case in which this substituent is fairly bulky, like the isopropyl group. With this object we synthesized 2,4,5-triisopropyl-α-methylstyrene. The starting material for the synthesis was 2', 4', 5'-triisopropylacetophenone, which was prepared from 1,2,4-triisopropylbenzene and acetyl chloride in presence of aluminum chloride in 62.1% yield. The 2', 4', 5'-triisoprophylacetophenone was then treated with the Grignard reagent derived from methyl iodide, but it was not found possible to introduce a methyl group in this way. Shorygin's method was then tried, and this was successful. The 2', 4', 5'-triisopropylacetophenone was treated with sodium and methyl iodide, and vacuum distillation without isolation of the intermediate product yielded 2,4,5-triisopropyl-α-methylstyrene, a colorless mobile liquid having a powerful aromatic odor and boiling at 110-111° (5 mm).

2,4,5-Triisopropyl-α-methylstyrene did not polymerize when heated at 100° for 100 hours in presence of benzoyl peroxide and when heated at 160° for 50 hours in absence of benzoyl peroxide. After treatment in this way, the original substance was recovered unchanged. Ionic catalysts were tried, also without success – after treatment in presence of aluminum chloride (1% on the amount of 2,4,5-triisopropyl-α-methylstyrene), the original monomer was recovered unchanged.

The absence of ability to undergo radical and ionic polymerization indicates that in 2,4,5-triisopyl-α-methylstyrene large steric effects operate and prevent the mutual approach of two vinyl groups which is necessary for reaction to occur. These steric-hindrance effects – or steric factors – in this case evidently include both a screening effect, and also a blocking effect, which is exerted by the two substituents on the double bond of the vinyl group.

In 4-tert-butyl-2,6-dimethylstyrene, which we investigated previously, there are two methyl groups ortho to the vinyl group, and the resulting blocking of the double bond led to loss in ability to polymerize by the radical mechanism, while the ability to polymerize in presence of ionic catalysts remained, ionic polymerization being much less sensitive

to the action of steric hindrance – as we have shown previously [6, 7].

Hence, a small substituent, such as a methyl group, when directly attached to the doubly-bound carbon, has a greater inhibiting effect on the polymerization process than two similar groups in the ortho positions of the phenyl group of the substituted styrene.

EXPERIMENTAL

2', 4', 5'-Triisopropylacetophenone. Aluminum chloride (25 g) was added in small portions to a cooled stirred mixture of 30 g of 1,2,4-triisopropylbenzene, 15 g of acetyl chloride, and 100 ml of tetrachloroethane. The mixture was set aside overnight, heated in a water bath for one hour, and poured into dilute hydrochloric acid to effect decomposition. The organic layer was separated in a separating funnel, and then washed – first with water, then with dilute sodium carbonate solution, and finally several times with water. The washed solution was dried with sodium sulfate, tetrachloroethane was distilled off, and the residue was vacuum-distilled. The fraction boiling at 156-162° (25 mm) was collected and recrystallized from alcohol; the yield was 22.5 g (62.1%).

2', 4', 5'-Triisopropylacetophenone forms long white needles having sharp odor of frankincense. It melts at 106-107° [9].

2,4,5-Triisopropyl-α-methylstyrene. A mixture of 20 g of 2', 4', 5'-triisopropylacetophenone, 40 g of methyl iodide, 18 g of granular sodium, and 200 ml of ether was prepared in a round-bottomed flask fitted with reflux condenser. As reaction was very slow, 1 ml of ethanol was added, and the reaction then became fairly vigorous. When the reaction slowed down, the flask was heated in a water bath for 60-90 minutes. The ether layer and suspended sodium derivative was decanted from the sodium. The mixture of sodium and sodium derivative that remained was shaken several times with ether, and the suspension of sodium derivative in ether was decanted; in this way the whole of the sodium derivative was extracted. The ether extracts were combined, and the sodium derivative was decomposed with water. The ether layer was separated in a separating funnel and washed – first with water, then with dilute hydrochloric acid, and finally several times with water. The ethereal solution was dried with anhydrous sodium sulfate, and the ether was distilled off. The residue was vacuum-distilled, and the fraction boiling at 114-118° (6 mm) was collected.

2,4,5-Triisopropyl-α-methylstyrene is a colorless highly mobile liquid having a fairly strong aromatic odor and boiling at 110-111° (5 mm). It is readily soluble in organic solvents and is insoluble in water. It has d_4^{20} 0.863; n_D^{20} 1.4870; Found MR 81.37; Calculated MR 81.26.

SUMMARY

1. 2,4,5-Triisopropyl-α-methylstyrene was synthesized.
2. It was found that 2,4,5-triisopropyl-α-methylstyrene will undergo neither radical nor ionic polymerization.

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BRIEF COMMUNICATIONS

PREPARATION OF p-TERPHENYL

B. M. Mikhailov and P. M. Aronovich

The known methods for the synthesis of p-terphenyl do not give the completely pure hydrocarbon in satisfactory yield – either they give high yields of inadequately pure hydrocarbon, or they give the pure substance, but in very low yield. For example, p-terphenyl can be prepared in 70% yield by the condensation of N,N'-p-phenylenebis[N-nitroacetamide] with benzene [1], but the product, after distillation at 0.001 mm and crystallization, has a low melting point. According to Braun [2], an almost quantitative yield of terphenyl can be attained by heating p-dicyclohexylbenzene with bromine. However, even after crystallization from benzene and distillation over sodium, the product melts at 209°. Dehydrogenation and simultaneous dehydration of 1,4-diphenyl-1,4-cyclohexanediol in presence of selenium [3] also gives inadequately pure p-terphenyl – after repeated sublimation in a high vacuum the substance melts at 210°.

Pure p-terphenyl (m.p. 213°) was prepared by Basford [4] by the dehydrogenation of 4-cyclohexylbiphenyl with selenium, but the author gives no indication of the yield. Dehydrogenation and decarboxylation of 3,6-diphenyl-4-cyclohexene-1,2-dicarboxylic anhydride (prepared by the condensation of 1,4-diphenyl-1,3-butadiene with maleic anhydride) [5] also gives the pure hydrocarbon (m.p. 211.5-212.5°), but in low yield.

We have worked out a method for the preparation of p-terphenyl by the dehydrogenation of p-dicyclohexylbenzene with selenium, and this enables us to obtain p-terphenyl of high purity in 66% yield. Since dehydrogenation with selenium proceeds only at the interface between the layers, the reaction rate can be considerably increased by agitation of the mixture. However, even then, reaction is rather slow. When a mixture of p-dicyclohexylbenzene and selenium was heated at 320° for 100 hours, the yield of p-terphenyl after a single crystallization from benzene was 73% (m.p. 210-212°). The product had a grayish tinge owing to admixture of colloidal selenium; it was purified quite readily by chromatography of its benzene solution on alumina. The resulting hydrocarbon formed completely colorless crystals, m.p. 212-213°.

In the procedure described below, in order to reduce the amount of solvent required it is recommended that the chromatography should be carried out on the hot benzene solution. However, the chromatography can be carried out on cold benzene solutions and also on solutions of p-terphenyl in other solvents, such as carbon tetrachloride.

EXPERIMENTAL

The dehydrogenation of p-dicyclohexylbenzene – which was prepared by Corson and Ipatieff's method [6] – was carried out in a long-necked round-bottomed flask or wide stainless-steel vessel. The neck of the flask or opening of the steel vessel was closed by a stopper carrying a two-way adapter. The side tube of the adapter was connected to an Ivitsky vessel containing caustic potash solution (for the absorption of hydrogen selenide) A stirrer passed through the vertical tube of the adapter. A mixture of 50 g (0.21 mole) of p-dicyclohexylbenzene (m.p. 97-99°) and 100 g (1.27 g-atoms) of selenium was prepared in the reaction vessel. The vessel was placed in a bath of Wood's metal, the bath was heated to 320°, and the stirrer was set in motion. The mixture was stirred at a bath temperature of 320-330° for 90-100 hours (with some interruptions), and a test sample was then taken from the upper layer of the reaction mixture. The sample was dissolved in hot benzene, the resulting solution was filtered, the filtrate was evaporated to dryness, and the melting point of the residue was determined. In such a test, reaction can be regarded as substantially complete when the sample melts completely at not below 203° (corrected).

When reaction was complete, the hot mixture was poured into a porcelain basin (in a fume cupboard!). When it was cool, it was ground and boiled with 800 ml of benzene. The hot solution was filtered through a heated Buchner funnel; unchanged selenium (about 20 g) remained on the filter (such selenium can be used in further experiments). The p-terphenyl that precipitated when the solution cooled was filtered off and washed with 20 ml of benzene. It was

pressed off (a dried sample melted at 210-212°) and dissolved in 1100 ml of boiling benzene. The resulting solution was chromatographed on 100 g of active alumina. In order to prevent the crystallization of the p-terphenyl during the chromatography process, the column was fitted with a hot-water jacket, which was maintained at 65-70°. When the p-terphenyl solution had passed through, the column was washed twice with hot benzene (about 100 ml), and the liquid passing through was collected in the receiver containing the main solution. One-half of the solvent was distilled from the mixture of crystals and solution, and the residue was cooled and filtered. The precipitate was washed three times with 20-ml portions of benzene and dried. The product, amounting to 31.5-32 g (65-66%), consisted of white crystals, m.p. 212-213°.

SUMMARY

A method has been developed for the preparation of pure p-terphenyl.

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ORGANOBORON COMPOUNDS

COMMUNICATION 3. PREPARATION OF THE ISOBUTYL ESTERS OF PHENYLPROPYL - AND BUTYLPHENYL BORINIC ACIDS

B. M. Mikhailov and P. M. Aronovich

By the action of phenyllithium on diisobutyl benzeneboronate, we prepared isobutyl diphenylborinate in 71% yield. Further study of the reaction between esters of benzeneboronic acid and other organoboron compounds showed that these reactions permit the preparation of previously undescribed alkylarylborinic esters. For example, by the action of propyllithium and of butyllithium on diisobutyl benzeneboronate, the isobutyl esters of phenylpropyl – and butylphenylborinic acids were prepared. These esters, like those of dibutylborinic [1] and diphenylborinic [2] acids, are difficult to hydrolyze. In the air they rapidly undergo change, being converted into benzeneboronic acid; it is evident that oxidation occurs and is accompanied by the hydrolysis of the benzeneboronic ester formed.

EXPERIMENTAL

Isobutyl Phenylpropylborinate. At – 50° to – 70° 46.8 g (0.2 mole) of diisobutyl benzeneboronate, diluted with 50 ml of ether, was added with stirring over a period of 30-40 minutes to a solution of propyllithium prepared at 0° from 32 g of propyl bromide, 3.5 g of lithium, and 200 ml of ether. The mixture was stirred for five hours at -70°, and then set aside overnight. On the next day the solution, which contained a little white precipitate, was saturated with dry hydrogen chloride. The greater part of the ether was distilled off, and the precipitate of lithium chloride and bromide was filtered off.

The precipitate was washed with 15 ml of benzene, and solvent and isobutyl alcohol were distilled from the filtrate under reduced pressure at temperatures up to 80-90°. Lithium salts were again filtered off, and the liquid was vacuum-fractionated through a column. The yield of isobutyl phenylpropylborinate, b.p. 87-90° (3 mm), was 22.8 g (55.8%). After a second distillation the ester boiled at 86-87° (3 mm) and had d_4^{20} 0.8943.

Found %: C 76.53; H 10.12; B 5.27
$C_{13}H_{21}OB$. Calculated %: C 76.49; H 10.37; B 5.30

Isobutyl Butylphenylborinate. Reaction was between 0.2 mole of diisobutyl benzeneboronate and 0.2 mole of butyllithium, the conditions being as described above. The yield of isobutyl butylphenylborinate, b.p. 96-97° (3 mm) and d_4^{20} 0.8894, was 29.4 g (67.4%).

Found %: C 77.03; H 10.64; B 4.63
$C_{14}H_{23}OB$. Calculated %: C 77.07; H 10.62; B 4.96

The syntheses of these esters were carried out in an atmosphere of dry nitrogen.

SUMMARY

It is shown that it is possible to prepare esters of mixed alkylarylborinic acids.

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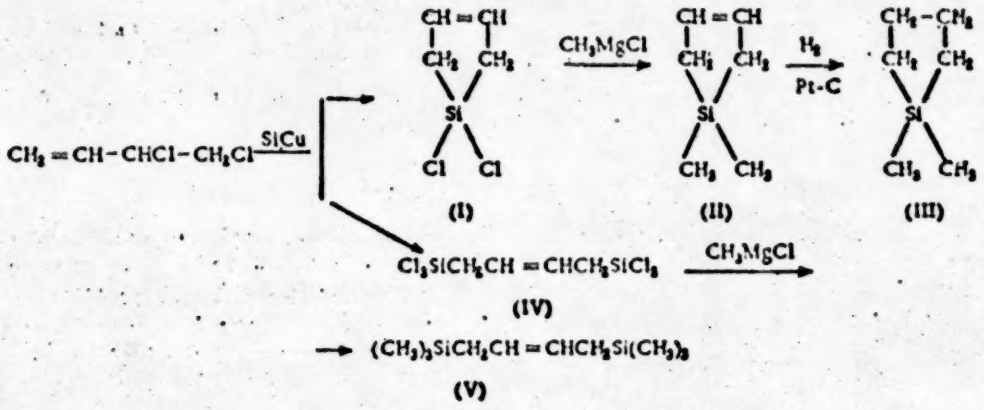
SYNTHESIS OF 1,1-DICHLOROSILACYCLOPENT-3-ENE

A. D. Petrov, G. I. Nikishin, N. P. Smetankina, and Yu. P. Egorov

There have been no reports of the preparation of unsaturated cyclic compounds containing a silicon atom and a double bond in the ring. All of the known saturated 4-, 5-, 6-, and 7-membered ring compounds containing silicon in the ring have been prepared by organometallic synthesis [1-6], with the exception of the trisilacyclohexane derivative of formula $[CH_2-SiCl_2]_3$, formed by the reaction of CH_2Cl_2 with silicon [7].

In a study of the behavior of 3,4-dichloro-1-butene in the direct synthesis, we found that in addition to 1,1,1,6,6,6-hexachloro-1,6-disilahex-3-ene (IV) the unsaturated heterocyclic compound 1,1-dichlorosilacyclopent-3-ene (I) was formed (the compounds are named in accordance with the Amsterdam nomenclature [8]. The formation of these compounds was evidently preceded by allyl rearrangement of 3,4-dichloro-1-butene to 1,4-dichloro-2-butene:



The structures of (II), (III), and (V) were confirmed by their Raman spectra. Thus, in the spectrum of (III) the following intense lines were found: 399 (5), 593 (10), 852 (4sh), 945 (2), 1022 (2), 1252 (3) cm^{-1} which coincide with the frequencies for 1,1-dimethylsilacyclopentane, which has been determined previously [2]. The spectrum of (II) contains a few intense lines, which may indicate the symmetrical character of its structure. The frequency of 915 cm^{-1} is probably an analog of symmetrical pulsational vibration of the ring [at 852 cm^{-1} in (III)]. An increase in frequency is observed also in alicyclic compounds: cyclopentane 986 cm^{-1}, cyclopentene 896 cm^{-1}. The C = C frequency (1610 cm^{-1}) is very close for that of the double bond in cyclopentene (1611 cm^{-1}). In the spectrum of (V) the C = C frequency is 1650 cm^{-1}, i. e. is higher than when the bond is in the α,β-position with respect to the silicon (1630 cm^{-1}). This fact, and also the absence of frequencies in the region of 3000-3100 cm^{-1}, attributable to a $=CH_2$ group, favors the structure (V) rather than $(CH_3)_2SiCH_2CH(Si(CH_3)_2)-CH=CH_2$. It is interesting to note that among the products of direct synthesis from 1,4-dichloro-2-butene, the compound (I) was again found, though in smaller amount.

EXPERIMENTAL

Direct Synthesis. A stream of 3,4-dichloro-1-butene (416 g) was passed at the rate of 23 g per hour through a glass tube (d = 40 mm, l = 600 mm) filled with pieces of Si – Cu alloy (Si ~ 80%; Cu ~ 20%) and placed in an electric tube furnace working at a temperature of 300 ± 10°. The product (280 g) was condensed by means of a water condenser and was then fractionated. Two fractions were obtained: 43.6 g (15.3%) of Fraction I, b.p. 128-136°, corresponding to 1,1-dichlorosilacyclopent-3-ene, b.p. 135°, d_4^{20} 1.2190; n_D^{20} 1.4782; MR_D 35.56; $MR_{D\,calc.}$ 36.2

Found: C 30.42; H 3.96; Cl 47.65; Si 17.95

$C_4H_8SiCl_4$. Calculated: C 31.37; H 3.95; Cl 46.32; Si 18.35

and 25 g (9%) of Fraction II, b.p. 240-243°, corresponding to 1,1,1,6,6,6-hexachloro-1,6-disilahex-3-ene, b.p. 243 d_4^{20} 1.4115, n_D^{19} 1.4879; MR_D 65.92; $MR_{D\,calc.}$ 65.00

Found: C 15.40; H 2.16, Cl 65.76; Si 17.24

$C_4H_6Si_2Cl_6$. Calculated: C 14.87; H 1.87, Cl 65.86; Si 17.39

Replacement of Chlorine by Methyl in the direct-synthesis products was effected with aid of CH_3MgCl. To the stirred ethereal solution of the Grignard reagent, which was prepared from 19.3 g (0.82 mole) of magnesium and 14.2 g (0.582 mole) of methyl chloride, the direct-synthesis product (I) or (IV) was added, the amounts taken being 33.1 g (0.176 mole) of (I) and 21 g (0.065 mole) of IV) •. After the reactants had been mixed, the reaction mixtures were boiled for 9-10 hours, and the products were isolated in the usual way.

The yield of 1,1-dimethylsilacyclopent-3-ene was 9.72 g (39.4%), and it had b.p. 100.5-101° (741-744 mm); d_4^{20} 0.8067; n_D^{23} 1.4433; MR_D 36.91; $MR_{D\,calc.}$ 36.94

Found: C 63.81; H 10.91; Si 24.76

$C_6H_{12}Si$. Calculated: C 64.2; H 10.78; Si 25.02

Raman spectrum (cm^{-1}): 183 (4b, background), 214 (2), 310 (4b), 411 (5), 620 (7), 730 (3b), 915 (5sh), 950 (1), 1100 (4), 1206 (4), 1258 (1), 1405 (5 b) 1610 (4 sh), 2894 (10 b), 2965 (8), 3024 (5).

1,1,8,8-Tetramethyl-2,7-disilaoct-4-ene was obtained in 34.7% yield (4.5 g); it had b.p. 187.5-188.5°; d_4^{20} 0.7789; n_D^{19} 1.4398; MR_D 67.81; $MR_{D\,calc.}$ 67.22

Found: C 60.15; H 12.12; Si 27.87

$C_{10}H_{24}Si_2$. Calculated: C 59.91; H 12.07; Si 28.02

Hydrogenation. A mixture of 6 g of (II), 0.1-0.2 g of platinized charcoal (5% Pt), and 20 ml of methanol was prepared in a hydrogenation flask. The flask was shaken mechanically while hydrogen was passed in from a gas holder for four hours. Almost the whole of the theoretical amount of hydrogen added within the first hour (1100 ml; theory requires 1200 ml). The reaction product $(CH_3)_4Si(CH_2)_4$, after distillation and chromatographic purification on silica gel, had the following constants: b.p. 107°, d_4^{20} 0.7871; n_D^{20} 1.4328. The literature [2, 5] gives b.p. 104.9-105° (742 mm); d_4^{25} 0.7938; n_D^{25} 1.4348; b.p. 107° d_4^{25} 0.780; n_D^{25} 1.4335.

SUMMARY

It is shown that, in direct synthesis from 3,4-dichloro-1-butene, not only 1,1,1,6,6,6-hexachloro-1,6-disilahex-3-ene, but also 1,1-dichlorosilacyclopent-3-ene may be formed.

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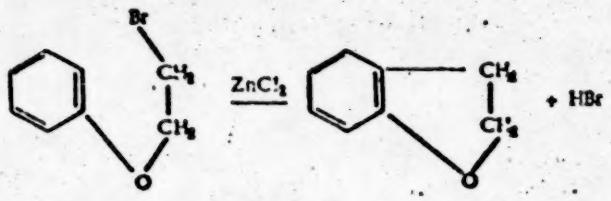
REACTIONS OF 2-BROMOETHYL PHENYL ETHER IN PRESENCE OF ZINC CHLORIDE AND A MIXTURE OF ZINC AND ALUMINUM CHLORIDES

E. N. Karaulova and G. D. Galpern

Rindfuss [1] described the synthesis of 2,3-dihydrobenzofuran (II) by the cyclization of 2-phenoxyethanol, and also of 2-bromoethyl phenyl ether (I), in presence of zinc chloride:



(I) (II)

The apparent simplicity of this synthesis attracted our attention. Repetition of the described synthesis yielded a product of b.p. 87-90° (17.5 mm) and n_D^{20} 1.542 [for 2,3-dihydrobenzofuran Rindfuss gives b.p. 88-90° (18 mm) and n_D^{20} 1.543]. However, further investigation showed that the product was not 2,3-dihydrobenzofuran, but phenol. Such physicochemical characteristics as boiling point, refractive index, and density are very similar for unpurified moist phenol and for 2,3-dihydrobenzofuran (the difficulty of preparing phenol in a high degree of purity is well known). Both 2,3-dihydrobenzofuran and phenol give violet colors with ferric chloride in presence of sulfuric acid. 2,3-Dihydrobenzofuran differs considerably from phenol in elementary composition, but, unfortunately, Rindfuss does not give the 2,3-dihydrobenzofuran.

EXPERIMENTAL

We took a mixture of 76.6 g of the ether (I) and 8 g of freshly fused, finely ground zinc chloride and refluxed it for two hours. Hydrogen bromide was evolved slowly and the boiling point (thermometer in the mixture) fell from 220° to 200°. The reaction products were vacuum-distilled (there was a very small amount of resinous residue). The distillate was washed with water and with 10% caustic soda solution, and was then dried and redistilled, three fractions being collected:

Fraction I, b.p. 51° (34 mm), 90° (26 mm); yield 10.51 g. Redistillation at atmospheric pressure yielded 6.4 g of a substance having b.p 129-134° and n_D^{20} 1.5378. The bromine content was 82.36%, and the value calculated for $C_2H_4Br_2$ is 83.57% (the dibromoethane contained some phenol impurity).

Fraction II, b.p. 83-90° (17.5 mm) – mainly 87-90° (17.5 mm); yield 7.87 g. Redistillation at atmospheric pressure gave a product boiling at 181-185° and having $n_D^{22.6}$ 1.542. When allowed to stand it crystallized and was found to melt at 39°. It was distilled once more and analyzed.

Found %: C 76.43; H 6.48
C_8H_8O. Calculated %: C 76.59; H 6.38

Fraction III, b.p. 210-230° (21 mm); m.p. 34.5°; yield 17.50 g. This was identified by a mixture melting point test as unchanged ether (I).

When, in similar experiments, the reaction mixture was refluxed for five hours, its boiling point continued to fall, and finally attained 155°, the boiling point of phenyl vinyl ether. When heating was continued still further the whole mass polymerized and there was extensive resinification. Further experiments with zinc chloride of various origins and with mixture of zinc and aluminum chlorides gave qualitatively the same results.

The greatest amount of phenol was formed when the ether (I) reacted in presence of equal amounts of zinc chloride and aluminum chloride (containing ferric chloride impurity). A mixture of 40.6 g of the ether 1.4 g of zinc chloride, and 4 g of aluminum chloride was heated for 2 hours 30 minutes and then treated as described above. The products were dibromoethane (3.66 g), phenol (7.63 g), and unchanged ether (I) (7.88 g). In none of the experiments did we succeed in detecting the presence of 2,3-dihydrobenzofuran among the products.

The results that we have obtained can be explained on the assumption that hydrogen bromide is first eliminated from the ether (I) when this is heated with zinc chloride (or its mixture with aluminum chloride):

$$C_6H_5OCH_2CH_2Br \xrightarrow[-HBr]{ZnCl_2} C_6H_5OCH=CH_2 \longrightarrow (C_6H_5OCH=CH_2)_n + HBr$$

At the high temperature the resulting phenyl vinyl ether rapidly polymerizes. In presence of zinc chloride the unchanged ether (I) reacts with hydrogen bromide.

$$C_6H_5OCH_2CH_2Br + HBr \xrightarrow{ZnCl_2} C_6H_5OH + BrCH_2CH_2Br.$$

We were unsuccessful also in an attempt to prepare 2,3-dihydrobenzofuran by the cyclization of 2-phenoxyethanol in presence of zinc chloride, of phosphoric oxide, or of a mixture of zinc and aluminum chlorides. It appeared that the first stage of the process consisted mainly in the dehydration of the phenoxyethanol. The water eliminated would then bring about the partial hydrolysis of zinc and aluminum chlorides with formation of hydrogen chloride. The further course of the reaction would then be as described above.

SUMMARY

When 2-bromoethyl phenyl ether was heated with zinc and aluminum chlorides, phenol and dibromoethane were formed, and apparently also phenyl vinyl ether and its polymers.

Contrary to Rindfuss' view, 2,3-dihydrobenzofuran is not formed under these conditions; nor is it formed when 2-phenoxyethanol is heated with zinc chloride, with phosphoric oxide, or with a mixture of zinc and aluminum chlorides.

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CHLORINATION OF DODECANE •

V. A. Nekrasova and N. I. Shuikin

The object of this investigation was to determine the conditions required in the synthesis of chloro derivatives of dodecane. The experiments were carried out in the apparatus described in our previous communication on the chlorination of undecane [1].

There is very little information in the literature on the chlorination of dodecane. Mabery [2] chlorinated dodecane in diffused light: the monochlorododecane that he obtained boiled over a wide range, 142-153° (80 mm), and he regarded the fraction boiling at 150-160° (80 mm) as dichlorododecane. The yields of the chloro derivatives were not given.

EXPERIMENTAL

As starting material for the preparation of chloro devivatives of dodecane we used the ligroin fraction of straight-run Crimean petroleum. Normal hydrocarbons were separated from their isomers and from cyclic hydrocarbons via the urea complex [3], and they were then subjected to precision fractionation. The isolated dodecane had the following properties: b.p. 215.5-217° (755 mm); d_4^{20} 0.7489; n_4^{20} 1.4218. Dodecane for use in control experiments (372 g) was synthesized from hexyl bromide by the Wurtz method, and its properties were as follows: b.p. 216-217° (758 mm); d_4^{20} 0.7487; n_D^{20} 1.4216; found MR 57.76, calculated $C_{12}H_{26}$ MR 57.62.

The chlorination of dodecane was carried out – both in vapor phase and in liquid phase – in presence of nitrogen dioxide. The molar ratio of dodecane and chlorine was 1 : 1 in all experiments, and chlorine was supplied at 1200 ml per hour. By way of example we shall describe briefly the results of the fractionation of the products obtained in an experiment on the vapor-phase chlorination of dodecane. At the above-stated molar ratio of reactants and rate of passage of chlorine, 85 g of dodecane was chlorinated at 400° and 83 g of chlorination product was obtained. The product was fractionated, and yielded:

Fraction I, B.p. 243-245° (758 mm); 37.0 g(44.6%); n_D^{20} 1.4380; d_4^{20} 0.8614; Cl 17.49%

Fraction II, B p. 255-257° (758 mm); 23.7 g(28.5%); n_D^{20} 1.4425; d_4^{20} 0.8670; Cl 17.43%;

Found MR 62.47; calculated for $C_{12}H_{25}Cl$ MR 62.48

Fraction III, B.p. 257-259°; 17.4 g (21%)

Residue 4.9 g (5.9%).

Comparison of the constants with reported values [4] indicated that Fraction I consisted of secondary monochloro derivatives; Fraction II corresponded to 1-chlorododecane; and Fraction III corresponded to a mixture of dichloro derivatives. The structure of the primary monochlorododecane was established by its hydrolysis to dodecyl alcohol (b.p. 255-257° at 758 mm) [5], which was converted by oxidation with alkaline hydrogen peroxide into lauric acid:

$$CH_3(CH_2)_{10}CH_2Cl \rightarrow CH_3(CH_2)_{10}CH_2OH \rightarrow C_{11}H_{23}COOH.$$

The acid so obtained melted at 44.3° and boiled at 223-224° (99-100 mm); these constants are close to the reported values [6]. The results of the vapor-phase chlorination of dodecane at various temperatures are given in the table.

At 420° the vapor phase chlorination of dodecane resulted in much decomposition and the formation of a charred residue.

We considered it desirable to study also the liquid-phase chlorination of dodecane in presence of a small amount

• Senior laboratory worker Z. V. Popova took part in the experimental work.

of nitrogen dioxide (2% on the weight of hydrocarbon) at a temperature close to the boiling point of the hydrocarbon (215-216°), chlorine being passed into the flask containing liquid dodecane at the rate of 1200 ml per hour. By way of example we shall give the results of the fractionation of the chlorination products obtained in one experiment. Under the conditions indicated above 85 g of dodecane yielded 99.7 g of chloro derivatives. Fractionation at 756 mm gave the following fractions:

Fraction I. B.p. 243-245°; 44.9 g (45%); n_D^{20} 1.4380; d_4^{20} 0.8614; Cl 17.49%

Fraction II. B.p. 255-257°; 19.9 g (18%); n_D^{20} 1.4425; d_4^{20} 0.8670; Cl 17.43%

Fraction III. B.p. 257-259°; 29.9 g (30%)

Residue 6.98 g (7%).

TABLE

Vapor-phase Chlorination of Dodecane in Presence of Nitrogen Dioxide

Expt. No.	Experimental temperature (°C)	Yield (%) on the amount of dodecane that reacted			
		1-Chlorododecane	Secondary mono-chlorododecanes	Dichloro derivatives	Residue
4	390	27.3	46.2	20.8	5.7
7	400	28.5	44.6	21.0	5.9
11	410	28.2	44.3	21.5	6.0
14	420	25.4	42.5	24.3	9.8

Fraction I corresponded in properties to secondary monochloro derivatives; Fraction II was 1-chlorododecane; Fraction III was a mixture of dichloro derivatives; and the residue apparently consisted of higher chlorination products.

An examination of our results on the liquid- and vapor-phase chlorination of dodecane indicates that it is most expedient to carry out the chlorination (not only of this hydrocarbon, but also of most other hydrocarbons of higher molecular weight) in the liquid phase in presence of nitrogen dioxide, since at high temperatures of 420° and higher the chloro derivatives formed undergo rapid decomposition under the conditions of vapor-phase chlorination. The presence of small amounts (2%) of nitrogen dioxide in the reaction mixture facilitates the initiation of the chain reaction – the formation of a free dodecyl radical in accordance with the scheme that we proposed in the preceding communication [1].

SUMMARY

1. The reaction of dodecane with chlorine in presence of nitrogen dioxide at high temperature (390-420°) was studied.

2. The optimum conditions were found for the formation of 1-chlorododecane in the vapor and liquid phases in presence of nitrogen dioxide.

3. In the chlorination of hydrocarbons containing 12 or more carbon atoms at 420°, it is desirable to carry out the reaction in the liquid phase in presence of nitrogen dioxide.

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CATALYTIC DEHYDROGENATION OF ISOPENTANE

N. I. Shuikin, T. P. Dobrynina, E. A. Timofeeva, and Yu. P. Egorov

The considerable amounts of pentane and isopentane that are available from the petroleum industry make it necessary to consider the question of their rational utilization. In previous papers [1, 2] we gave some results on the dehydrogenation of pentane: we showed that treatment of pentane at 500-550° can yield catalyzates containing 22-26% of pentenes. The object of the present investigation was to find the conditions under which isopentenes are obtained in the catalytic dehydrogenation of isopentane, and to determine their structures. As a result of our experiments we have succeeded in establishing the optimum conditions for the dehydrogenation of isopentane and in finding an alumina-chromia catalyst promoted by potassium oxide (90.7 mole-% Al_2O_3, 5.6 mole-% Cr_2O_3, 3.7 mole-% K_2O) in presence of which a catalyzate containing 38% of isopentenes (33% on the amount of original isopentane) is formed.

EXPERIMENTAL

The dehydrogenation reaction was carried out under atmospheric pressure at 527°. The catalysis tube contained 25 ml (17.5 g) of catalyst. Isopentane (b.p. 27.8-28.3°; n_D^{20} 1.3540; d_4^{20} 0.6200) was supplied in 10-ml portions from a spray buret at a space velocity of 0.5 $hour^{-1}$. After the fourth portion had been passed (40 ml), the catalyst was regenerated by treatment with air for 2 hours at 550°. The catalyst could be used in the reaction for 160 hours without appreciable loss of activity. A combined catalyzate obtained in experiments carried out under these conditions boiled over the range 20.0-148.0° (corrected) and had the following properties: n_D^{20} 1.3690, d_4^{20} 0.6340, iodine number 137.8, content of unsaturated hydrocarbons 37.9%. It was obtained in 87.0% yield. Analysis of the gas: hydrogen 85.2%, paraffin hydrocarbons 13.8%, unsaturated hydrocarbons 1.0%. The catalyzate (174.3 g) was fractionated through a 40-plate column. The results of the fractionation and the properties of the fractions are given in the table.

Investigation of Catalyzate Fractions. Fraction I. This contains isopentane and 3-methyl-1-butene. This is confirmed not only by the properties of the fraction, but also by Raman spectrum investigation. The value of the iodine number indicates that the 3-methyl-1-butene content is 13.2% (1.5% on the whole catalyzate).

Fraction II. Apart from unchanged isopentane, this contains approximately equal amounts (as determined from the Raman spectrum) of 3-methyl-1-butene and 2-methyl-1-butene. The value of the iodine number indicates that the total content of unsaturated hydrocarbons in this fraction is 10.8% (about 5.4% of each of the isopentenes, or 2.9% of each on the whole catalyzate).

Fraction III. Aanlysis by the Raman spectrum method indicates that this fraction contains isopentane, 2-methyl-1-butene, 2-methyl-2-butene, and probably 1-pentene. 2-Methyl-2-butene predominates among the unsaturated hydrocarbons. The total content of unsaturated hydrocarbons in the fraction is 40% (1.4% on the whole catalyzate).

Fraction IV. The value of the iodine number indicates that this fraction contains 82.6% of unsaturated hydrocarbons (2.6% on the whole catalyzate), which probably consist mainly of 2-methyl-2-butene. It is possible that it contains very small amounts of 2-methyl-1-butene. The saturated part of the fraction was not investigated, but the boiling range indicates that it consists mainly of n-pentane.

Fraction V. This fraction, and also Fraction VI, was isolated by fractionation from a small flask fitted with a column. It contains 61.1% of unsaturated hydrocarbons (1.7% on the whole catalyzate), mainly 2-methyl-2-butene, but also a little cis-2-pentene (determined by the Raman spectrum method).

Fraction VI. Most of this fraction came over at 110°. Its infrared absorption spectrum was determined, and it indicated that the fraction consists mainly of toluene; a little 2-methyl-2-butene (0.6% on the fraction) is also present. These results are confirmed by the properties of the fraction.

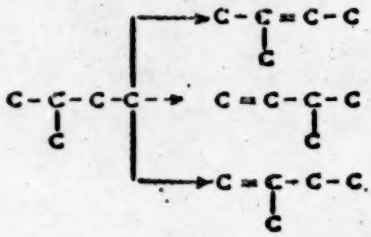
Hence, in the dehydrogenation of isopentane in presence of an alumina-chromia catalyst promoted by potassium oxide, a mixture of isopentenes is obtained. It consists mainly of 2-methyl-2-butene, and contains also the other two possible isopentenes – 3-methyl-1-butene and 2-methyl-1-butene. Other substances found in the catalyzate in small quantities are 1-pentene, 2-pentene, toluene, and, apparently, n-pentane. On the basis of our results we consider that

TABLE

Properties of Fractions of Combined Isopentane Catalyzates

Fraction No.	Boiling limits in °C (corrected)	Amount (%)	n_D^{20}	d_4^{20}	Iodine number	Content of unsaturated hydrocarbons (% by weight)
I	20.0-25.0	11.7	1.3560	0.6223	48.0	13.2
II	25.0-30.0	50.9	1.3580	0.6230	39.2	10.8
III	30.0-36.0	3.5	1.3775	0.6485	145.0	40.0
IV	36.0-39.0	29.8	1.3815	0.6530	300.0	82.6
V	39.0-43.5	2.8	1.3990	0.6728	221.3	61.5
VI	43.5-148.0	1.2	1.4850	0.8426	2.2	0.6
Residue	–	0.1	1.5110	–	–	–

the main reactions of 2-methylbutane under the conditions of our experiments are:



As regards the formation of aromatic hydrocarbons, this is a matter for further investigation.

SUMMARY

A catalyst was found for the dehydrogenation of isopentane to isopentenes, namely, a mixture of the oxides of chromium, aluminum, and potassium. The optimum conditions for its action were determined.

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* T.p. = C. B. Translation pagination

SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

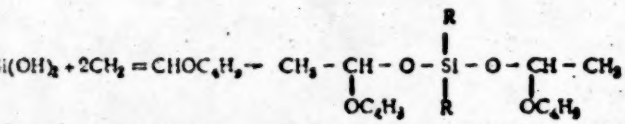
COMMUNICATION 2. REACTIONS OF DIETHYL- AND DIPHENYL-SILANEDIOLS WITH VINYL ETHERS

M. F. Shostakovsky, D. A. Kochkin, and V. M. Rog

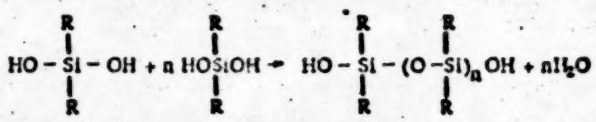
This paper describes the further investigation of organosilicon compounds containing hydroxyl groups. It was shown previously that trialkyl- or triaryl-silanols R_3SiOH react with alkyl vinyl ethers with formation of organosilicon acetals $CH_3CH(OR)(OSiR_3)$ [1-3]. In the present investigation we have studied the reactions of dialkyl- and diaryl-silanediols (the examples taken being diethyl- and diphenyl-silanediols) with vinyl ethers with the object of preparing organosilicon diacetals:

(R is alkyl or aryl)

No acetals of such structure have been described in the literature. Reaction between butyl vinyl ether and diethyl- and diphenyl-silanediols proceeds with the formation of several by-products, as indicated by the following equations.



(1)



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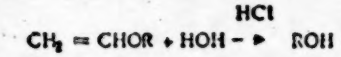

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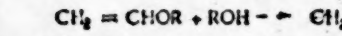


(4)

Apart from organosilicon diacetals, the products isolated included acetaldehyde dibutyl acetal and alkyl- or aryl-substituted polysiloxanes, which confirms the reaction scheme given above. The optimum conditions for the formation of organosilicon diacetals were found to be as follows: considerable excess of the vinyl ether, use of acids as catalysts, and heating of the reaction mixture for 90-120 minutes 60°. The reaction is then displaced in the direction of preferential formation of diacetal (Equation 1), and the accompanying reactions (Equations 2-4) are largely suppressed. The structure of the diacetal obtained from diethylsilanediol was confirmed by hydrolysis with 5% sulfuric acid, which proceeds according to the following equation:

EXPERIMENTAL •

Preparation of the Diacetal Bis (1-butoxyethoxy)diethylsilane. A mixture of 12.0 g of diethylsilanediol (m.p. 92.0-92.5°)•• 50 g of butyl vinyl ether (b.p. 93.0-94.0°; n_D^{27} 1.4018; d_4^{20} 0.7792), and one drop of concentrated hydrochloric acid was prepared in a sealed tube, which was heated for 90-120 minutes at 60° and then set aside overnight. The mixture was neutralized with potassium carbonate and fractionated, the following fractions being collected:

Fraction I, B.p. 60-68° (12 mm): n_D^{20} 1.4100; d_4^{20} 0.8273; 4.2 g

Fraction II, B.p. 126-133° (6 mm); n_D^{20} 1.4260; 11.5 g

Fraction III, high-boiling products.

Butyl vinyl ether was collected in a trap. Fraction I was acetaldehyde dibutyl acetal [5]. Refractionation of Fraction II yielded 10 g (37%) of the diacetal bis (1-butoxyethoxy) diethylsilane, b.p. 127-129° (5 mm); n_D^{20} 1.4270; d_4^{20} 0.9010; found MR 91.49; calculated for $C_{14}H_{34}SiO_4$ MR 90.90; found M (in benzene) 303.5; 310.0; calculated M 320.5.

Found %: C 60.56; 60.63; H 11.42; 11.34; Si 8.36, 8.44

$C_{14}H_{34}SiO_4$. Calculated %: C 60.00; H 11.32; Si 8.75

The high-boiling product was found to be polydiethylsiloxane. The acetal is a clear liquid of ethereal odor, readily soluble in ether and alcohol.

Hydrolysis of Bis (1-butoxyethoxy)diethylsilane. The diacetal (0.5 g) was heated with 50 ml of 5% sulfuric acid in a sealed tube in a boiling water bath until a homogeneous solution was obtained (3-4 hours). The contents of the tube were transferred to a measuring flask and diluted with water to 200 ml. Titration by the bisulfite method gave 94.99% and 96.3% of the theoretical amount of acetaldehyde.

Reaction of Butyl Vinyl Ether with Diphenylsilanediol. A mixture of 5 g of diphenylsilanediol (m.p. 139°)•••, 50 g of butyl vinyl ether, 20 ml of ether, and one drop of hydrochloric or sulfuric acid was prepared in a sealed tube, which was heated in a boiling water bath until the diphenylsilanediol dissolved completely (a few hours). The mixture was neutralized and fractionated, the following products being obtained:

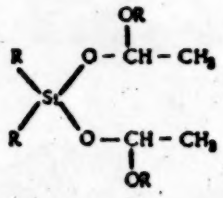
Fraction I, B.p. 55° (1.5 mm); n_D^{20} 1.4089; d_4^{20} 0.8259; 2.5 g

Fraction II, high-boiling residue

Fraction I was acetaldehyde dibutyl acetal [5]. It was not found possible to isolate the diacetal diethylbis-(1-phenoxyethoxy) silane $(CH_3CHOC_6H_5O)_2Si(C_2H_5)_2$ by fractionation of the high-boiling residue, owing to its thermal instability. In order to determine the acetaldehyde equivalent of the reaction products, the high-boiling residue was hydrolyzed in the manner described above. The values found for the acetaldehyde content were 83.46% and 82.83% of the theoretical amount. We consider that the high-boiling residue was a mixture of the diacetal diethylbis (1-phenoxyethoxy) silane and the macromolecular condensation product of diphenylsilanediol. The nature of the compounds obtained is under investigation.

SUMMARY

1. The reactions of diethyl- and diphenyl-silanediols with butyl vinyl ether were investigated. It was shown that oxygen-containing organosilicon compounds could be obtained, namely diacetals of general structure:



• Junior scientific worker A. M. Gutman participated in the work.

•• Diethylsilanediol was prepared by the hydrolysis of dichlorodiethylsilane with N NaOH, and the dichlorodiethylsilane was prepared by direct synthesis from ethyl chloride [4].

••• Prepared by the hydrolysis of dichlorodiphenylsilane with N NaOH or N KOH. It was found that diphenylsilanediol was best crystallized from a mixture of ether and isopentane.

2. These diacetals were obtained only when an excess of the vinyl ether was used.

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OBITUARY

ALEKSANDR VASILYEVICH TROFIMOV

Aleksandr Vasilyevich Trofimov, senior scientific worker and one of the foremost members of the staff of the Vernadsky Institute of Geological and Analytical Chemistry of the USSR Academy of Sciences, died suddenly at Vilyuisk at 8 a. m. on June 19, 1955, while out on an expedition.

A. V. Trofimov was born in Moscow in 1899. In 1923, while still a student and before completion of his course at the Timiryazev Agricultural Academy, Trofimov began an investigation of the chemistry and physical chemistry of soils in the General Agriculture Department. During this period and the period following graduation (up to 1930), he worked as a chemist in the Timiryazev Agricultural Academy and published a series of papers on moisture relations and structure in soils; he studied the penetration of water into soils, the reaction of soils as a function of moisture, and acid exchange in solutions in contact with soils.

In 1930 Trofimov took up work at the State Oceanography Institute (reorganized later as a part of the All-Union Fishery and Oceanography Research Institute- VNIRO), where he studied the physical chemistry of the sea; chemical composition of sea water, submarine actinometry, and iodiferous seaweeds. These investigations are still extensively cited, not only here, but also abroad.

Later, Trofimov obtained some very valuable experience in precision instrument-making at the Moscow Experimental Station for the Construction of Control and Measuring Instruments and also, subsequently at the Air Force Research Institute. He showed himself to have the qualities of a first-class instrument maker, and he became well-versed in the intricacies of this complicated work.

After demobilization in 1944 from the Red Army, Trofimov took up a post as senior scientific worker at the Vernadsky Institute of Geological and Analytical Chemistry of the USSR Academy of Sciences. Since then Trofimov's scientific activities have been wholly associated with a new field of knowledge – the geochemistry of isotopes. His investigations took up three main directions: the geochemistry of stable isotopes of carbon, sulfur, oxygen, and argon; the determination of the absolute geological age of recent formations by the carbon method; and investigations on meteorites by the isotope method. In order to carry out these investigations, Trofimov designed unique apparatus (mass-spectrometers and counters for the determination of C-14). As a result of his investigations Trofimov made some important geochemical generalizations. On the basis of the identity in mean isotopic composition of the carbon of the primary igneous rocks of the earth and the carbon of meteorites, he confirmed experimentally the hypothesis of the genetic identity of the substance of the earth and that of meteorites. The same conclusion was confirmed by investigation of the isotopic composition of sulfur from meteorites and from the earth's crust. He provided experimental confirmation of V. I. Vernadsky's hypothesis of the preponderance of organic carbon over carbonate carbon in the earth's crust.

Trofimov's investigations on the isotope exchange of the oxygen of carbonate indicated the great stability of these deposits in geological time. This conclusion is very important for the paleothermometric method, which is now used in climatology and geology.

Trofimov worked on the determination of the absolute geological age of sedimentary formations with the aid of C-14; in particular, he worked on the sedimentary rocks of the Yakutsk Republic. He determined the geological ages of the soils of the Taimyr peninsular and the time of the existence of the Taimyr mammoth.

The premature death of A. V. Trofimov came at the very height of his creative work. He was a true Soviet scientist – his life devoted entirely to science. In his person there was a happy combination of the brilliant experimentalist and the creator of broad generalizations.

He was well versed in the most varied fields of science, and at the same time he had a very original turn of mind. He was a highly talented investigator. Trofimov was a very loyal colleague, who will never be forgotten by those who met him. He freely shared his knowledge with others and he made great demands

on himself. He shone out as an example of an indefatigable worker, a highly conscientious man, distinguished by a rare modesty.

The death of Aleksandr Vasilyevich Trofimov is a grievous loss to science, and it brings the deepest sorrow to all his colleagues and friends.

Vernadsky Institute of Geological and
Analytical Chemistry of the USSR
Academy of Sciences

SALUTATION TO ALEKSANDR NAUMOVICH FRUMKIN

on the Occasion of his Sixtieth Birthday

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences, Division of Chemical Sciences congratulate you on the occasion of your sixtieth birthday and of the completion of forty years of scientific activity.

Your many and varied physicochemical investigations—particularly in the field of electrochemistry—form a very significant contribution to science.

We hope that you will enjoy good health and will continue in your successful creative work.

DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE U S S R

EDITORIAL BOARD OF THE BULLETIN OF THE ACADEMY OF SCIENCES OF THE U S S R, DIVISION OF CHEMICAL SCIENCES

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EFFECT OF THE METHOD OF MAKING MODIFYING ADDITIONS ON THE PROPERTIES OF OXIDE CATALYSTS

G. M. Zhabrova and E. A. Fokina

The way in which additives are distributed at the surface and in the body of a catalyst and the possibility of interaction between additives and the catalyst are matters of great interest for the understanding of the laws governing the action of additives on catalysts. It was considered probable that change in the method of introducing additivescan result in a change in their distribution in the catalyst and have a substantial effect on the catalytic properties of the catalyst.

As a model reaction of the oxidation-reduction type we made use of the decomposition of hydrogen peroxide in presence of magnesium oxide [1]. It was found that, in the pure state, magnesium oxide has only moderate catalytic activity, and this facilitated the detection of positive effects attributable to additions. Stannic oxide was selected as additive; in the pure state this substance has a negligible catalytic effect The rate of decomposition of hydrogen peroxide was determined gasometrically, the procedure being similar to that described previously [1].

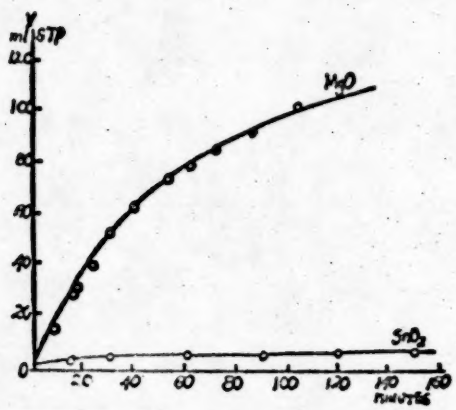

Fig. 1. Kinetic curves for the decomposition of hydrogen peroxide over magnesium oxide and over stannic oxide (reaction temperature 45°)

Fig. 1 shows kinetic curves for the decomposition of hydrogen peroxide over pure magnesium oxide and over pure stannic oxide. It will be seen that the activity of the former is about 35-40 times as great as that of the latter. As stannic oxide is introduced into the magnesium oxide in small amounts (0.01-6.4%), the effect of the simple summation of the activities of the two oxides can be neglected.

For the introduction of stannic oxide into magnesium oxide, the following three methods were used:

1. Impregnation of prepared magnesium oxide with solutions of tetraphenyltin. Magnesium oxide is impregnated with chloroform solutions of tetraphenyltin at various concentrations, dried at 100-120°, and calcined for one hour at 600° in a quartz vessel in an atmosphere of air. Pyrolysis of tetraphenyltin gives phenyl radicals and atomic tin, which is oxidized by atmospheric oxygen to stannic oxide (Series 1).

2. Impregnation of prepared magnesium oxide with solutions of stannic chloride. Magnesium oxide is impregnated with aqueous stannic chloride solutions of various concentrations, and the stoichiometric amount of 20% sodium carbonate solution is added to the resulting paste. The catalyst samples prepared in this way are washed, dried, and calcined for four hours at 450° in a quartz vessel in an atmosphere of air (Series 2).

3. Coprecipitation of magnesium and tin salts with sodium carbonate solution, the basic carbonates formed being washed, dried, and calcined at 450° (Series 3).

The amount of stannic oxide introduced was determined by polarography and spectrum analysis.

For our study of the catalytic properties of the magnesium oxide samples containing additions of stannic oxide it was necessary to select a method of determining the relative activities of the samples. It was established that the course of the decomposition of hydrogen peroxide is satisfactorily described by a first-order equation. The value of